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A Group Theoretical Method of Treating Polyhedral Molecules with Spin State Eigenfunctions

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A GROUP THEORETICAL METHOD OF TREATING POLYHEDRAL MOLECULES WITH SPIN STATE EIGENFUNCTIONS

BY

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A GROUP THEORETICAL METHOD OF TREATING POLYHEDRAL MOLECULES WITH SPIN STATE EIGENFUNCTIONS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

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INTRODUCTION

The object of this thesis is to examine a basic deficiency in the valence bond theory as developed by Heitler, London, Slater and Eyring and to offer an alternate general approach that leads to a greater reduction of the secular determinant for some molecular structures.

It is observed that in the formation of independent valence bond eigenfunctions, there exists an implicit assumption that one is working with planar or near-planar molecules. But when a polyhedral structure is considered, it is found that the independent valence bond eigenfunctions are no longer suitable basis functions for the symmetry group of the structure. This is best seen in the fact that the functions which correspond to the Kekulé and Dewar type structures are not independent in the polyhedral case.

An alternate method is developed for obtaining eigenfunctions. Symmetry operators are used to form linear combinations of spin state eigenfunctions having eigenvalue zero for S_z. These symmetry eigenfunctions are formed under different irreducible representations, thus reducing the secular determinant. Linear combinations of these symmetry eigenfunctions are made using symmetry arguements so that each new linear combination is an eigenfunction of the total spin angular momentum operator, S^2. Those final eigenfunctions having an eigenvalue of zero for S^2 are solved to obtain the ground state

energy.

Square, hexagonal, tetrahedral, octahedral, and cubical configurations are considered by this method.

Spin State Eigenfunctions

A primary characteristic of the spin state theory is that it attempts to consider all the interaction terms found in the Hamiltonian, including the electron interaction term, once the Born-Oppenheimer approximation has been made. This straightforward approach to the problem tends to become excessively complex for many electron systems (i.e., ten or more electrons) because of the increasing number of ways in which the electrons may interact. For simplicity, it is assumed in the following discussion that there is only one valence electron associated with each atom.

Consider a system of n atoms each having one valence electron, where (1, 2, 3, . . . n) is an abbreviation for the coordinates X_1, Y_1, Z_1; X_2, Y_2, Z_2; . . . X_n, Y_n, Z_n) of the electrons. Let (a, b, c, . . . n) be eigenfunctions, e.g., atomic orbitals, which describe each electron localized in the potential field of its respective atom.

It follows from elementary wave theory[1] that an orbital eigenfunction, f, describing a state of the system may be formed by taking the product of functions such as a(1), b(2), . . . where a(1) indicates that electron "1" is associated with the field "a".

Thus

$$f = a(1)b(2)c(3) \ldots n(n) \qquad (1)$$

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[1]Duffey, Physical Chemistry, (New York: McGraw-Hill Book Co., Inc., 1962), pp. 96-97.

This may be done because f^2 measures probability density.

Now each electron has a spin associated with it. The projection of the spin along any axis, z, has eigenvalues S_z where

$$S_z = \pm \frac{1}{2} \quad \frac{h}{4\pi} \tag{2}$$

The eigenfunctions having these values for S_z are referred to as α and β, respectively. One may associate α and β values with each electron. One such association would be

$$\begin{pmatrix} 1 & 2 & 3 & 4 & \ldots & n \\ \alpha & \beta & \alpha & \beta & \ldots & \beta \end{pmatrix} \tag{3}$$

For this association a spin function, A, may be written as

$$A = 1(\alpha)2(\beta)3(\alpha)4(\beta)\ldots n(\beta) \tag{4}$$

Now, the orbital function, f, and the spin function, A, may be combined into another product, t, which will more completely describe the system.

$$t_{\alpha,\beta,\alpha\ldots\beta} = fA = a(1\alpha)b(2\beta)\ldots n(n\beta) \tag{5}$$

Now electrons are indistinguishable, so the function given by Eq. (5) is not unique. By permuting the electrons one may produce n! other equally valid functions, and all should contribute to the final

eigenfunction with equal weight[2]. Thus, one might use the linear sum of these terms.

$$t = \sum_P P\ a(1\alpha)b(2\beta) \ldots . n(n\beta) \qquad (6)$$

where P interchanges all possible electron pairs.

However electrons obey the Pauli Exclusion Principle. This states that only those functions which are antisymmetric with respect to an exchange of electrons are allowable[3]. The antisymmetric character of the function may be introduced by including the operator $(-1)^P$ in Eq. (6). Thus

$$t\alpha, \beta, \ldots \beta = \sum_P (-1)^P P\ a(1\alpha)b(2\beta) \ldots . n\ (n\beta) \qquad (7)$$

Rather than assign α and β values directly to each electron, one may associate these values directly with each orbital eigenfunction. Each electron, then, takes on the value of α or β which is associated with its host orbital. Following this plan, Eq. (7) becomes

$$t\alpha, \beta, \alpha, \ldots \beta = \sum_P (-1)^P Pa\alpha(1)b\beta(2)c\alpha(3) \ldots . n\beta(n) \qquad (8)$$

Eq. (8) may be written in determinantal form as

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[2]Jaffé and Orchin, Theory and Application of Ultraviolet Spectroscopy, (New York: John Wiley and Sons, Inc., 1962), pp. 40-41.

[3]Duffey, op. cit., pp. 124-125.

$$\chi_{\alpha,\beta,\alpha,\cdots\beta} = \begin{vmatrix} \bar{a}(1) & b(1) & \bar{c}(1) & \cdots & \bar{n}(1) \\ \bar{a}(2) & b(2) & \bar{c}(2) & \cdots & \bar{n}(2) \\ \bar{a}(3) & b(3) & \bar{c}(3) & \cdots & \bar{n}(3) \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ \bar{a}(n) & b(n) & \bar{c}(n) & & \bar{n}(n) \end{vmatrix} \qquad (9)$$

where a bar over the orbital indicates the presence of α while its absence indicates β. This type of function, Eq. (9), is referred to as a Slater determinant or a spin state function[4]. There are 2^n possible spin state functions for a n-electron problem since each column of the Slater determinant may be assigned either an α or β value. It may be noted that interchanging electrons interchanges rows of the determinant, thus changing its sign. This preserves the antisymmetric character of the eigenfunction.

Each of the 2^n spin state functions describes a possible physical state of the system. Thus, they may be used to form a 2^nth order secular determinant, $\left| H_{ij} - S_{ij} E \right| = 0$, which will, in theory, enable one to find the corresponding energy states of the system. But since matrix elements between certain states are zero, one need not consider such a large determinant.

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[4]J. C. Slater, Phys. Rev., 38, 1109 (1931).

Operators Needed to Reduce the Secular Determinant

There are two methods available which will enable one to reduce the 2^nth order secular determinant to several determinants of lower order. The first method is analogous to that used in atomic physics where one determines operators which commute, or nearly commute, with the Hamiltonian operator; and then, using these operators, one forms eigenfunctions having different eigenvalues. This method is stated more explicitly in the following two well known theorems[5].

Theorem A: If two operators R_1 and R_2 commute, there exists a set of functions which are simultaneously eigenfunctions of both operators.

Theorem B: If R_1 is an operator which commutes with an operator R_2 (where both are Hermitian), and f_1 and f_2 are eigenfunctions of R_2, then the interaction element $\int f_1^* R_2 f_2 d$ vanishes unless $a_1 = a_2$, where a_1 and a_2 are the eigenvalues of f_1 and f_2.

In quantum mechanical systems one may begin with functions, t_i, each of which describes a possible physical state of the system. These are eigenfunctions of the Hamiltonian operator, H, whose eigenvalues, E_i, are approximations to the discrete energies of the system. One seeks to obtain linear combinations of these functions which better describe the physical state of the system; that is, combinations which have eigenvalues for as many known physical quantities of the system as

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[5]Eyring, Walter, and Kimball, Quantum Chemistry (New York: John Wiley and Sons, Inc., 1944), pp. 34-37.

possible. The derived eigenvalues, E_j, for such combinations should be a more accurate set. By Theorem A, only operators which commute with the Hamiltonian operator may be used to form linear combinations. If such an operator, R_1 is found, then functions may always be formed which are eigenfunctions of both R and H. By Theorem B, there will be no interactions between eigenfunctions of R having different eigenvalues; thus, many elements in the secular determinant will vanish.

In atomic physics the operators M^2, M_z, S^2 and S_z are usually used[6] to reduce the secular determinant. However, M^2 and M_z only commute with the Hamiltonian when the system has spherical symmetry; therefore, they may not be used for most molecular problems. The operators S^2 and S_z may still be used. These operators commute with the Hamiltonian if one neglects spin interaction. They also commute with themselves. S^2 is the operator for the square of the total spin angular momentum of all n electrons.

$$S^2 = S_x^2 + S_y^2 + S_z^2 \tag{10}$$

And S_z is one of the components of the total spin momentum operator. It is defined by

$$S_z = \sum_{i=1} s_{zi} \tag{11}$$

where s_{zi} is the projection of the spin along any z axis for the ith

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[6]Eyring, Walter, and Kimball, op. cit., pp. 133-143.

electron in the system.

The second method of attacking the secular determinant is to utilize the symmetry properties of the system by the application of group theory. This method has been developed in a number of sources[7]. For the purpose of reducing the secular determinant, the theorem from group theory that is pertinent is given by Theorem C[8]

Theorem C: For an operator, like the Hamiltonian, which commutes with all the operations of the group, nondiagonal integrals $\int f_A H f_B d\tau$ vanish when f_A and f_B are basis functions for different irreducible representations.

Using spin state functions as basis functions for reducible representations, linear combinations called symmetry eigenfunctions may be formed which are basis functions belonging to irreducible representations. This is done by use of the standard group theoretical generating machine[9].

According to Theorems A and C the symmetry operators must commute with the Hamiltonian if the results are to be meaningful. Symmetry operators are either rotations or reflections or combinations of the two. Such operations merely bring a molecule into coincidence with itself by interchanging like particles. This has no effect on the

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[7]L. D. Crossman, M.S. Thesis, South Dakota State University, 1963.

[8]J. C. Slater, Quantum Theory of Molecules and Solids (New York: McGraw-Hill Book Co., Inc., 1963), pp. 333-334.

[9]D. P. Olsen, M.S. Thesis, South Dakota State University, 1963.

kinetic or potential energy terms describing a molecule; thus, the Hamiltonian is invariant under such operations and will commute with them.

It is important that the symmetry operators also commute with the operators S_z and S^2 because, in general, functions which are simultaneously eigenfunctions of S_z, S^2, and symmetry operator R will result in the greatest reduction of the secular determinant.

Formation of Valence Bond Eigenfunctions

The valence bond method, in effect, is to first make the spin state functions eigenfunctions of S_z and S^2 and then to combine these eigenfunctions by use of the symmetry operators so that the final functions will belong to different irreducible representations.

The spin state functions, Eq. (10), are first classified according to the net spin S_z of all n electrons. Each term in the expansion of a spin state function, t_i, is an eigenfunction of S_z with the same eigenvalue; thus, the sum is an eigenfunction. The corresponding eigenvalue is

$$S_z t_i = n_\alpha \left(+\frac{1}{2}\frac{h}{2\pi}\right) + n_\beta \left(-\frac{1}{2}\frac{h}{2\pi}\right) t_i$$

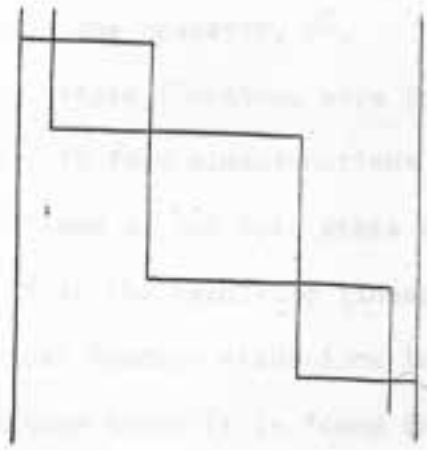
$$= (n_\alpha - n_\beta)\frac{h}{4\pi} t_i \qquad (12)$$

where n_α and n_β are the number of assigned α and β values in a term of t_i. It is obvious from this equation that a system of n electrons may have eigenvalues of S_z ranging from $\pm \frac{nh}{4\pi}$ for all α and β spins to zero for an equal number of α and β spins. The number of functions, t_i, capable of taking on each eigenvalue also varies. For example, in the four electron case there are $2^4 = 16$ spin state functions which break down according to eigenvalues as in Table 1.

Table 1.

Eigenvalues (in $h/2\pi$ units):	2	1	0	-1	-2
No. of Eigenfunctions	1	4	6	4	1

From Theorem B in the preceding section it is seen that when t_i and t_j are eigenfunctions having different eigenvalues, their interaction is zero, thus one can see that there will be considerable simplification of the secular determinant. In the four electron case, the determinant of order sixteen is reduced to a sixth order, two fourth orders, and two first orders.



$$= 0 \qquad (13)$$

One need not examine systems of all possible eigenvalues of S_z, but only those which correspond to the stable state of a system. One would suspect that as a general consideration a system is in its most stable state when the maximum number of stable bonds have been formed (although there are exceptions). Each stable bond contains an α, β electron pair according to the Pauli Exclusion Principle; thus, for an even number of electrons, the eigenfunctions to be considered have an eigenvalue of S_z equal to zero. Using this consideration, the four electron problem is reduced from a sixteenth order determinant to a sixth order determinant. Eyring gives a general rule[10] for the number

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[10] H. Eyring and G. E. Kimball, J. Am. Chem. Soc., 54, 3876 (1932).

of eigenfunctions, N′, corresponding to an eigenvalue of S_z.

$$N' = \frac{n!}{(n/2 + S)!\left(\frac{n}{2} - S\right)!} \tag{14}$$

A second effort can be made in reducing the problem by considering another physically observable quantity of the system, the eigenvalue corresponding to the operator, S^2.

The spin state functions were found to already be eigenfunctions of S_z; however, to form eigenfunctions of S^2, it is necessary to make linear combinations of the spin state functions. These new equations are formed so that the resulting linear combinations conform to two-electron chemical bonding situations in the molecule. From the treatment of elementary cases it is found that such combinations, called valence bond eigenfunctions will be eigenfunctions of S^2. Moreover, it is found that those bond eigenfunctions corresponding to different numbers of bonds have different eigenvalues of S^2.

In order to form the bond eigenfunctions, a function $\delta_{ab}(k)$ is assigned to each pair of orbitals in the molecule[11]. This function, $\delta_{ab}(k)$, has the value +1 if in the kth spin state function, the spin of a is α and the spin of b is β ; it has the value -1 if the spin of a is β and the spin of b is α ; it has the value of zero if a and b are associated with the same spin.

Suppose in the four electron case one wishes to write the bond

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[11]Eyring, J. of Chem. Phys., 1, 239 (1932)

eigenfunction describing the bonds between orbitals a and b and orbitals c and d. The required bond eigenfunction, $\Psi_{ab,cd}$, is given by

$$\Psi_{ab,cd} = \sum_{k=1}^{6} \delta_{ab}(k) \cdot \delta_{cd}(k)\, t_k \qquad (15)$$

The summation is from one to six because only spin state functions having an eigenvalue of zero are being considered, and, from Table 1, there are only six such functions in the four electron case.

By using equations similar to Eq. (15), all the bond eigenfunctions may be written down with the aid of the following spin state table.

Table 2.

	a	b	c	d
t_1	α	α	β	β
t_2	α	β	α	β
t_3	β	α	α	β
t_4	α	β	β	α
t_5	β	α	β	α
t_6	β	β	α	α

The two-bond eigenfunctions are

$$\begin{aligned} \Psi_{ab,cd} &= t_2 - t_3 - t_4 + t_5 \\ \Psi_{ac,bd} &= t_1 - t_3 - t_4 + t_6 \\ \Psi_{ad,bc} &= t_1 - t_2 - t_5 + t_6 \end{aligned} \qquad (16)$$

One-bond eigenfunctions may also be written. For example

$$\psi_{ab} = t_2 - t_3 + t_4 - t_5 \tag{17}$$

And the no-bond eigenfunctions may be written as

$$\psi = t_1 + t_2 + t_3 + t_4 + t_5 + t_6 \tag{18}$$

However, not all these eigenfunctions will be independent. The two-bond eigenfunctions may be related as

$$\psi_{ac,bd} = \psi_{ab,cd} + \psi_{ad,bc} \tag{19}$$

where the two on the right hand side are chosen as the independent functions.

All of the bond eigenfunctions are eigenfunctions of S^2. The two-bond eigenfunctions have the eigenvalue zero for S^2; the one-bond eigenfunctions have the value $1(1+1)h^2$ for S^2; and the no-bond eigenfunction has the eigenvalue $2(2+1)h^2$ for S^2 [12].

Now, because the interaction is zero when ψ_i and ψ_j are eigenfunctions having different eigenvalues, the sixth order secular determinant breaks down into one one-row determinant, one two-row determinant, and one three-row determinant. The two-row determinant is the determinant for the two bond eigenfunctions. Two bonds are the maximum number allowed in a four electron system; therefore, the energy of the ground state at the system should be given by the solution of

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[12] Eyring, Walter, and Kimball, op. cit., p. 237.

this determinant.

In conclusion, for the four electron problem, $2^4 = 16$ spin state functions were first considered. The number was reduced to six equations by choosing only those that had eigenvalue zero for S_z. The number was further reduced to two by taking linear combinations and choosing only those independent equations with eigenvalue zero for S^2.

These final equations could have been obtained immediately by making use of Rumers Rule[13] which states:

> "Arrange the orbitals in a circle, draw all the structures which contain the maximum number of bonds, but draw only those which contain no crossed bonds. The eigenfunctions corresponding to these structures are linear independent, and, as all bond eigenfunctions representing the maximum number of bonds can be expressed in terms of them, they form a complete set."

The Rumer diagrams for the four electron problem are given in Figure 1. The two upper diagrams produce the independent functions, $\Psi_{ab,cd}$ and $\Psi_{ad,bc}$. The lower diagram produces the dependent function, $\Psi_{ac,bd}$.

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[13] G. Rumer, Göttingen Nachr., 377 (1932)

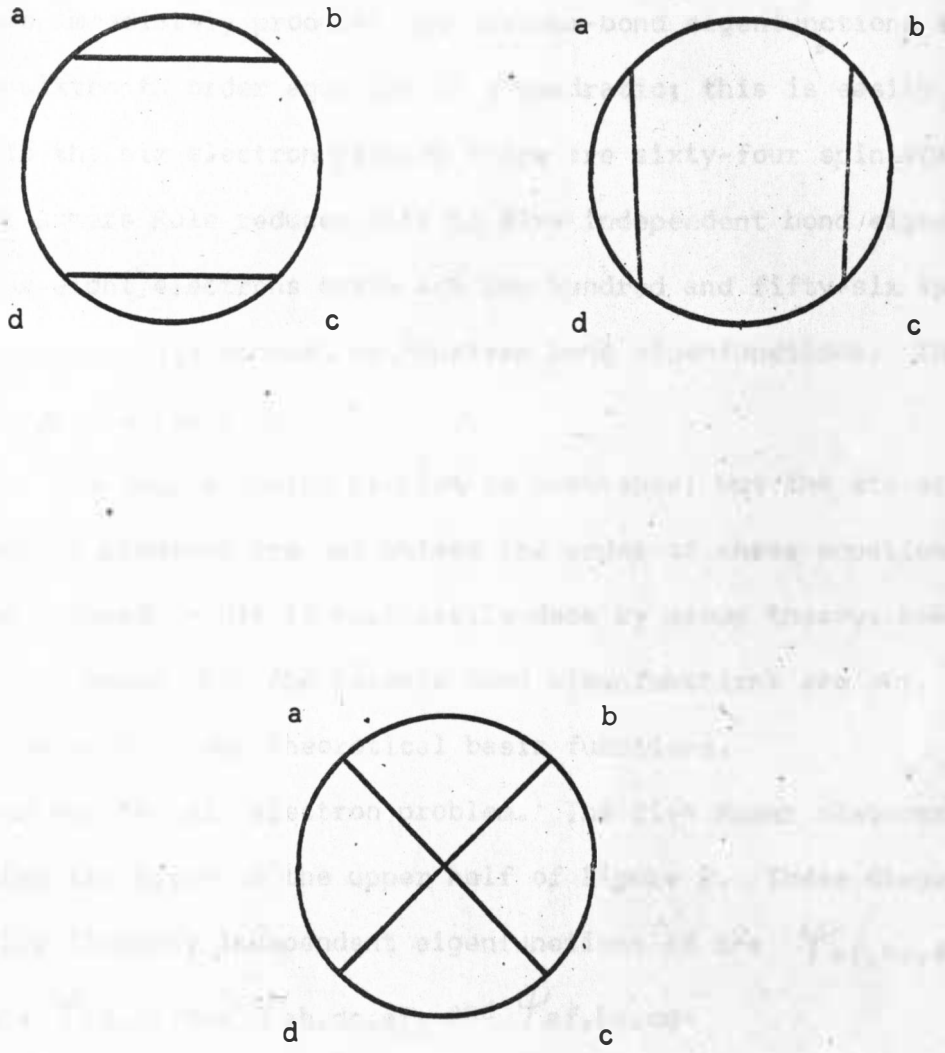

Figure 1. Rumer diagrams, four electron problem.

Limitations of Valence Bond Eigenfunctions

When the valence bond method is applied to polyelectron problems, the following results appear. In the four electron case, the use of Rumers Rule immediately produces two maximum-bond eigenfunctions and reduces a sixteenth order equation to a quadratic; this is easily solved. In the six electron problem there are sixty-four spin state functions; Rumers Rule reduces this to five independent bond eigenfunctions. For eight electrons there are two hundred and fifty-six spin state functions; this reduces to fourteen bond eigenfunctions. These results appear in Table 3.

Now, the four electron problem is tractable; but the six and eight electron problems are not unless the order of these equations can be further reduced. This is most easily done by group theory; however, investigation shows that the valence bond eigenfunctions are not, in general, desirable group theoretical basis functions.

Consider the six electron problem. The five Rumer diagrams for this problem are given in the upper half of Figure 2. These diagrams produce five linearly independent eigenfunctions of S^2: $\Psi_{af,bc,de}$, $\Psi_{ab,cd,ef}$, $\Psi_{ab,cf,de}$, $\Psi_{ab,dc,ef}$, and $\Psi_{af,be,cd}$.

Now, if the six electron problem is the benzene molecule, a near planar structure, then the five Rumer diagrams correspond to the two Kekulé and the three Dewar classical structures[14] of the benzene

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[14] L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill Book Co., Inc., 1935), pp. 374-380.

Table 3.

Number of Electrons	Number of Spin State Functions	Number of Spin State Functions with $S_z = 0$	Number of Valence Bond Functions with $S^2 = 0$
4	16	6	2
6	64	20	5
8	256	70	14
10	1024	252	42

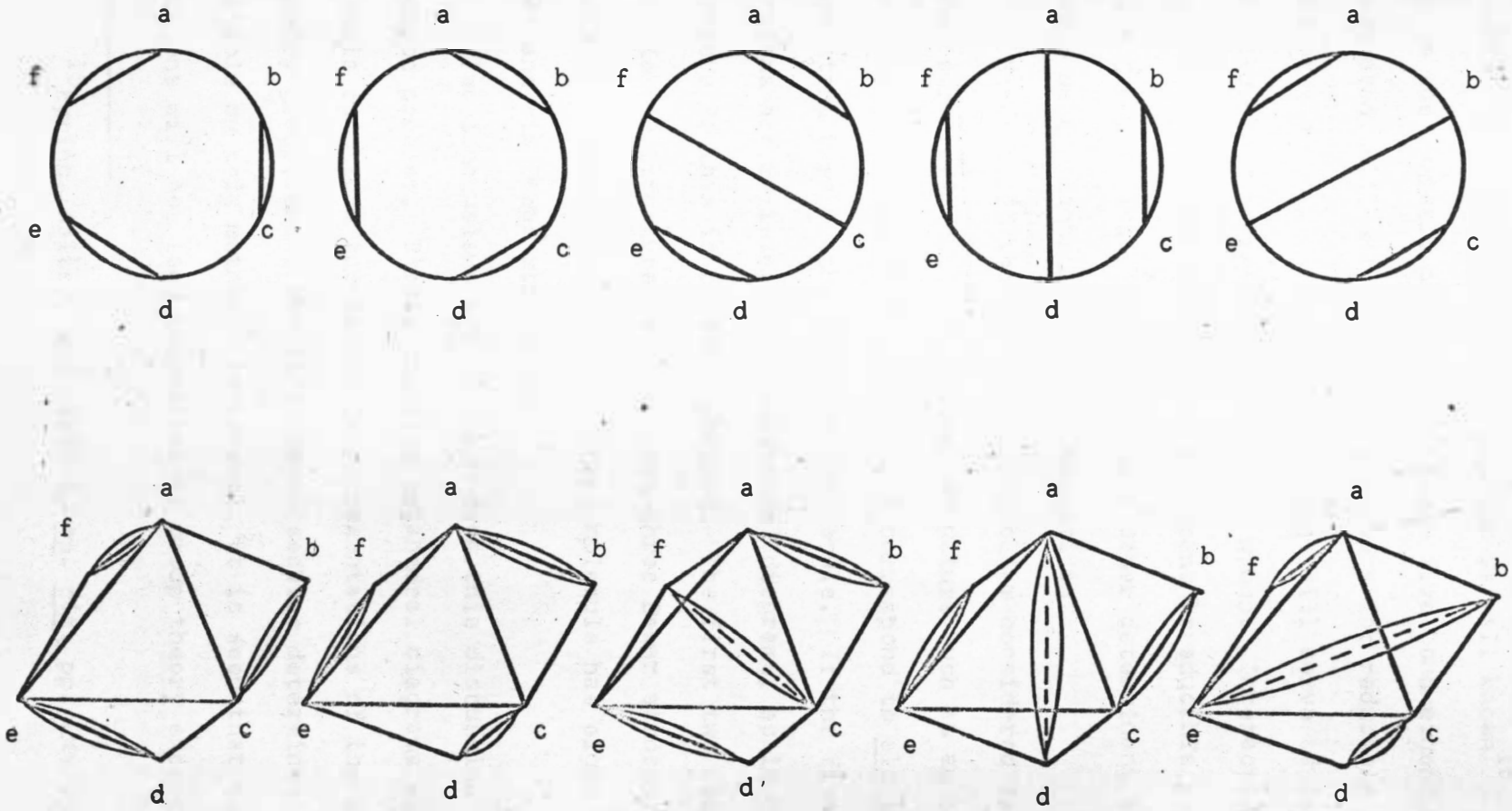

Figure 2. Upper: Rumer diagrams, six electron problem.
Lower: Corresponding valence bond structures, octahedren.

molecule. The solution of this problem is well known[15]. Benzene belongs to the symmetry group D_{6h}. These five bond eigenfuctions, as illustrated, will serve as basis functions for reducible representations of the group. Linear combinations will serve as basis functions for irreducible representations of the group. Interaction terms between eigenfuctions belonging to different irreducible representations of the group vanish. Thus, the fifth order determinant is reduced to two two-row determinants and one-row determinant.

However, if the six electron problem considered is not the planar structure, but a polyhedral structure such as an octahedron, then these five Rumer diagrams do not correspond to all the Kekulé and Dewar structures of the octahedral molecule. If the five bond eigenfunctions are represented on octahedral diagrams, as in the lower part of Figure 2, this is readily apparent. The first two diagrams are once again Kekulé structures and the last three Dewar structures. But inspection will show that an octahedral molecule has eight Kekulé structures and six Dewar structures.

Two conclusions may be drawn from this discussion of the six electron problem. First, the five octahedral diagrams will not serve as basis functions for reducible representations of the octahedral symmetry group; thus, the fifth order secular determinant remains untractable by this method. In general, it is seen that the valence bond functions will not lend themselves to group theory except for the

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[15]Eyring, Walter, and Kimball, op. cit. pp. 249-254.

special case where the Rumer diagrams form a basis for the same group as the atomic cores of the molecule. Secondly, the traditional Kekulé and Dewar "resonance" structures are not useful in building up a description of polyhedral molecules because the valence bond functions which correspond to such structures are no longer mathematically independent. That is, many polyhedral Kekulé and Dewar structures will correspond to Rumer diagrams having "crossed bonds."

In order to obtain the maximum reduction of the secular determinant for polyhedral molecules, one is forced to abandon the valence bond functions and find more satisfactory combinations of spin state functions. In doing so, the Kekulé and Dewar structures will disappear from the calculation. However, such structures are no longer considered as important as they once were by chemists[16-17], so their loss is not necessarily detrimental to the theory.

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[16]Linnett, The Electronic Structure of Molecules (London: Methuen and Co., Ltd., 1966)

[17]W. F. Luder, J. of Chem. Ed., 44, 206 (1967)

Formation of the Symmetry Eigenfunctions

In this method the spin state functions are first classified according to the net spin, S_z. Those eigenfunctions corresponding to an eigenvalue of zero for S_z are selected. These eigenfunctions are combined by use of the symmetry operators, and eigenfunctions are obtained which belong to different irreducible representations. Linear combinations of these eigenfunctions are made using symmetry arguments so that the linear combinations will be eigenfunctions of S^2.

When the valence bond functions were formed, it was shown that the spin state functions were eigenfunctions of S_z; and, when $n_\alpha = n_\beta$, the eigenvalue is zero. In the four electron case, there were six such functions; these are given in Table 2. Applying these to the tetrahedren, one obtains the six spin state configurations of Figure 4. Now, the spin state functions are independent, and under tetrahedral symmetry these six are basis functions for the reducible representations. Choosing a group appropriate to the tetrahedral symmetry, such as the C_{3v} group, the standard group theoretical generating machine[18] may be applied to produce symmetry eigenfunctions which are linear combinations of the six spin states. These linear combinations are basis functions for the irreducible representations of the group, and matrix elements between functions corresponding to different representations are zero,

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[18]Streitwieser, Molecular Orbital Theory, John Wiley and Sons, Inc., pp. 80-81, 1961.

as stated in Theorem C.

If the eigenfunctions corresponding to each irreducible representation are now examined to see if they are eigenvalues of S^2, it is found that in general they are not; however, simple linear combinations may be formed which are.

Two principles are used to combine the functions. First, only symmetry eigenfunctions having corresponding nodal surfaces are combined[19]. A nodal surface is established by determining the net spin distribution of all the spin states making up the symmetry eigenfunction. This is done by superimposing each contributing spin state configuration on the tetrahedral model. The resulting distribution will be analogous in shape to the s, p, d type of shape found in atomic orbitals. If a symmetry eigenfunction does not have the desired nodal surface, another partner spin state function is chosen from the symmetry eigenfunction and is applied to the generating machine. This is done until the symmetry eigenfunction possessing the desired nodal surface is generated.

The other principle used to help form eigenfunctions follows from the theorem that all symmetry functions formed under a given irreducible representation must be orthogonal[20]. Once a combination of functions is found that produces an eigenfunction of S^2, then any function orthogonal to this eigenfunction is found to also have an

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[19]D. P. Olsen, op. cit., pp. 35-39.

[20]Wigner, Group Theory (New York: Academic Press, 1959), pp. 117-118.

eigenvalue for S^2.

To determine the effect of S^2 on an eigenfunction, one may define S^2 as

$$S^2 = S_x^2 + S_y^2 + S_z^2 \tag{20}$$

Recalling the commutative rules

$$\begin{aligned} S_x S_y - S_y S_x &= ih S_z \\ S_y S_z - S_z S_y &= ih S_x \\ S_z S_x - S_x S_z &= ih S_y \end{aligned} \tag{21}$$

S^2 may be written as

$$S^2 = (S_x - iS_y)(S_x + iS_y) - hS_z \quad S_z^2 \tag{22}$$

The eigenfunctions to be considered have eigenvalue zero for S_z, so that

$$S^2 = (S_x - iS_y)(S_x + iS_y) \tag{23}$$

The two terms on the right may be expanded as

$$\begin{aligned} S_x + iS_y &= S_{x_1} + iS_{y_1} + S_{x_2} + iS_{y_2} \cdots \\ S_x - iS_y &= S_{x_1} - iS_{y_1} + S_{x_2} - iS_{y_2} \cdots \end{aligned} \tag{24}$$

where S_{x_1} and S_{y_1} are the operators for the x and y components of the spin of electron 1.

Since [21]

$$
\begin{aligned}
S_{x_1}\alpha(1) &= \frac{h}{4\pi}\beta(1) \\
S_{y_1}\alpha(1) &= \frac{ih}{4\pi}\beta(1) \\
S_{x_1}\beta(1) &= \frac{h}{4\pi}\alpha(1) \\
S_{y_1}\beta(1) &= \frac{ih}{4\pi}\alpha(1)
\end{aligned}
\tag{25}
$$

one has

$$
\begin{aligned}
(S_{x_1} + iS_{y_1})\alpha(1) &= 0 \\
(S_{x_1} + iS_{y_1})\beta(1) &= \hbar\,\alpha(1) \\
(S_{x_1} - iS_{y_1})\alpha(1) &= \hbar\,\beta(1) \\
(S_{x_1} - iS_{y_1})\beta(1) &= 0
\end{aligned}
\tag{26}
$$

Now the effect of the operator $(S_x + iS_y)$ on a spin state function, t_1, is to act on each spin part in turn, converting β to $\alpha\hbar$ and α to zero.

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[21] Glasstone, Laidler, and Eyring, The Theory of Rate Processes (New York: McGraw-Hill Book Co., Inc., 1941), p. 51.

Thus half of the terms produced will be zero. The other $\frac{n}{2}$ terms will contain one more α than β. Operating on <u>each</u> of these with $(S_x - iS_y)$ will convert α to β and β to zero; $\frac{n}{2}+1$ new terms will be produced, one of these will be t_1 itself. The other $\frac{n}{2}$ terms will correspond to a single interchange of an α,β pair. Operating on <u>all</u> $\frac{n}{2}$ terms will produce $\frac{n}{2}$ t_1's, and $\left(\frac{n}{2}\right)^2$ terms which differ from t_1 by a single interchange of an α,β pair. Each possible single interchange will appear once. Thus,

$$S^2 t_1 = (S_x - iS_y)(S_x + iS_y)t_1$$

$$= \sum_{\text{all } R'} R' t_1 + \frac{n}{2}\, t_1 \qquad (27)$$

where each R' causes a different single interchange. In practice, the application of the latter part of this equation greatly simplifies the task of establishing eigenvalues of S^2.

In general, each of the final eigenfunctions belonging to the same irreducible representation will be an eigenfunction of S^2 with a different eigenvalue. Thus, in most cases, the entire secular determinant will reduce to easily tractable equations of the first and second order.

Discussion of the Integrals

For quantum mechanical systems one may obtain approximations to the discrete energy levels of the system by solving a secular determinant[22]. The allowed energy levels are given by the roots, E, of the equation

$$\det \left| H_{AB} - S_{AB}E \right| = 0 \tag{28}$$

where

$$H_{AB} = \int \psi_A^* H \psi_B d\tau \tag{29}$$

and

$$S_{AB} = \int \psi_A^* \psi_B d\tau \tag{30}$$

If ψ_A and ψ_B are normalized eigenfunctions of S^2 with eigenvalues zero, as developed in the preceding section, then they are linear combinations of the spin state functions, t_i. Thus, the evaluation of equations such as Eq. (29) and Eq. (30) will ultimately involve only functions of the following types.

$$H_{ij} = \int t_i^* H t_j d\tau \tag{31}$$

$$H_{ii} = \int t_i^* H t_i d\tau \tag{32}$$

$$S_{ij} = \int t_i^* t_j d\tau \tag{33}$$

and

$$S_{ii} = \int t_i^* t_i d\tau \tag{34}$$

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[22] G. H. Duffey, op. cit., pp. 164-166.

A brief analysis of the nature of these functions follows, using the two electron problem as an example. Also, the four electron problem is considered to help develop rules for determining H_{ij} and H_{ii}.

The two spin state eigenfunctions for the two electron problem are

$$t_1(a\beta) = N\left[(a\alpha)_1(b\beta)_2 - (a\alpha)_2(b\beta)_1\right] \tag{35}$$

$$t_2(\beta\alpha) = N\left[(a\beta)_1(b\alpha)_2 - (a\beta)_2(b\alpha)_1\right] \tag{36}$$

where the fundamental orbitals a and b are each normalized to one, and N is the corresponding normalization constant for t_1 and t_2.

Substituting Eqs. (35) and (36) into Eq. (33) and expanding, yields

$$S_{12} = \iint t_1^* t_2 d\tau_1' d\tau_2' \tag{37}$$

$$= N^2 \iint \left[(a\alpha)_1(b\beta)_2 - (a\alpha)_2(b\beta)_1\right]^* \left[(a\beta)_1(b\alpha)_2 - (a\beta)_2(b\alpha)_1\right] d\tau_1' d\tau_2'$$

where $d\tau_1' = d\tau_1 dw_1$. The terms $d\tau_1$ and dw_1 are elements in orbital space and spin space, respectively. If the magnetic interaction between the spin and the orbital angular momenta is neglected, the spin and the orbital parts may be separated[23]. When Eq. (37) is expanded, the first term will be

$$\iint a_1 b_2 a_1 b_2 d\tau_1 d\tau_2 \int \alpha_1 \beta_1 dw_1 \int \beta_2 \alpha_2 dw_2 \tag{38}$$

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[23] Jaffé and Orchin, op. cit., pp. 158-159.

Now, the spin eigenfunctions α and β may be normalized to one and, because each corresponds to a different eigenvalue of S_z, they are orthogonal. That is

$$\int \alpha^2 dw = \int \beta^2 dw = 1 \tag{39}$$

and

$$\int \alpha\beta \, dw = 0 \tag{40}$$

Applying these conditions to Eq. (38) and integrating over the spin functions, the first and last terms of the expansion vanish and the middle terms are seen to be equivalent. The latter add, and the function becomes

$$S_{12} = -2N^2 \iint a_1 b_1 a_2 b_2 d\tau_1 d\tau_2$$

$$= -2N^2 \left[\int a_1 b_1 d\tau_1 \right]^2 = -2N^2 S_{ab}^2 \tag{41}$$

The term $S_{ab} = S$ is called the overlap integral between orbital function a and orbital function b. It will be different from zero only if a and b are nonorthogonal. The orbitals a and b are generally considered to be atomic orbitals, and atomic orbitals located on different nuclei are not orthogonal. The overlap for such orbitals may be as high[24] as 0.3. Neglecting the overlap integral results in a severe approximation which will become clearer when the H_{ij} integral is discussed. Explicit atomic overlap formulas may be found in the

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[24]Tinkham, op. cit., p. 224.

literature[25], but to include them in a complex problem requires the use of a computer[26].

Because the spin state functions are normalized to one, the value of the integral S_{ii} will also be one.

Substituting Eq. (35) into Eq. (32) yields

$$H_{11} = \iint t_1^* H t_1 \, d\tau_1' d\tau_2' \tag{42}$$

$$= N^2 \iint \left[(a\alpha)_1 (b\beta)_2 - (a\alpha)_2 (b\beta)_1 \right]^* H \left[(a\alpha)_1 (b\beta)_2 - (a\alpha)_2 (b\beta)_1 \right] d\tau_1' d\tau_2'$$

If one assumes that the Hamiltonian operator does not operate on the spin functions, the spins may again be separated and integrated. The integral becomes

$$H_{11} = N^2 \iint \left[(a_1 b_2) H (a_1 b_2) + (a_2 b_1) H (a_2 b_1) \right] d\tau_1 d\tau_2$$

$$= 2N^2 \iint (a_1 b_2) H (a_1 b_2) \, d\tau_1 d\tau_2 \tag{43}$$

Now, the Hamiltonian operator for the hydrogen molecule may be written

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{R_{A1}} - \frac{1}{R_{A2}} - \frac{1}{R_{B1}} - \frac{1}{R_{B2}} + \frac{1}{R_{AB}} + \frac{1}{r_{12}} \tag{44}$$

if one chooses the proper atomic units[27]. In the Hamiltonian the

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[25] R. S. Mulliken, C. A. Rieke, D. Orloff, J. Chem. Phys., 17, 1248 (1949).

[26] R. L. Oakland, M.S. Thesis, South Dakota State University, 1966.

[27] Tinkham, op. cit., p. 219.

subscripts, A and B, and 1 and 2, refer to the nuclei and electrons, respectively.

Substituting Eq. (44) into Eq. (43) yields

$$H_{11}=2N^2\iint(a_1b_2)\left[-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{1}{R_{A1}}-\frac{1}{R_{A2}}-\frac{1}{R_{B1}}-\frac{1}{R_{B2}}+\frac{1}{R_{AB}}+\frac{1}{r_{12}}\right](a_1b_2)d\tau \tag{45}$$

Integrating each term and rearranging yields

$$H_{11}=2N^2\left[-\frac{1}{2}\int a_1\nabla_1^2 a_1 d\tau_1-\frac{1}{2}\int b_2\nabla_2^2 b_2 d\tau_2-\int\frac{a_1^2}{R_{A1}}d\tau_1-\int\frac{b_2^2}{R_{B2}}d\tau\right]$$

$$+2N^2\left[-\int\frac{b_2^2}{R_{A2}}d\tau-\int\frac{a_1^2}{R_{B1}}d\tau+\frac{}{R_{AB}}+\iint\frac{a_1^2\,b_2^2}{r_{12}}d\tau_1 d\tau_2\right]$$

$$=2N^2\left[2E_{1S}(H)+J\right] \tag{46}$$

where $E_{1S}(H)$ is the Hamiltonian energy associated with an electron in an isolated hydrogen atom, and J is the direct or coulombic integral[28]. The integral J is zero when the atoms are infinitely far apart. As the atoms approach each other, J describes the coulomb energy attraction of the electrons of each atom for the nucleus of the other, and the Coulomb energy repulsion of the nuclei and of the electrons.

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[28]Eyring, Walter, and Kimball, op. cit., p. 214.

In a similar manner, substituting Eqs. (35), (36), and (44) into Eq. (31) yields

$$H_{12}=2N^2S\left[-\frac{1}{2}\int a_1\nabla_1^2 b_1 d\tau_1-\frac{1}{2}\int a_2\nabla_2^2 b_2 d\tau_2-\int\frac{a_1b_1}{R_{A1}}d\tau_1-\int\frac{a_2b_2}{R_{B2}}d\tau_2\right]$$

$$-2N^2\left[-S\int\frac{a_2b_2}{R_{A2}}d\tau-S\int\frac{a_1b_1}{R_{B1}}d\tau+\frac{S^2}{R_{AB}}+\iint\frac{a_1b_1a_2b_2}{r_{12}}d\tau\,d\tau\right]$$

$$=-2N^2(SE'+K) \qquad (47)$$

where S is the overlap integral and K is called the exchange integral[29]. Neither E' or K may be given an exact physical significance; however, the term (a_1b_1) is sometimes referred to as the "exchange charge density" in the overlap region. It is important to note that if the overlap integral is set equal to zero, the exchange integral will be positive; but if the overlap integral is included in the calculation, the exchange integral will generally be negative[30].

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[29] Tinkham, op. cit., pp. 223-226.

[30] Ibid., p. 227.

Determining Rules for Exchange and Coulomb Integrals

To help establish a workable system for calculating terms such as H_{ii} and H_{ij} consider two spin state functions for an n electron system.

$$t_i = \frac{1}{\sqrt{n!}} \sum_k (-1)^k P_k \left[(a\alpha)_1 (b\beta)_2 (c\beta)_3 \cdots (n\beta)_n \right] \tag{48}$$

$$t_j = \frac{1}{\sqrt{n!}} \sum_\ell (-1)^\ell P_\ell \left[(a\alpha)_1 (b\beta)_2 (c\alpha)_3 \cdots (n\beta)_n \right] \tag{49}$$

The term $1/\sqrt{n!}$ is the normalization constant when the overlap integral is neglected.

Substituting t_i and t_j into H_{ij}, given by Eq. (31), yields

$$H_{ij} = \frac{1}{n!} \int \left[\sum_k (-1)^k P_k \left[(a\alpha)_1 (b\alpha)_2 (c\beta)_3 \cdots \right] H \sum_\ell (-1)^\ell P_\ell \left[(a\alpha)_1 (b\beta)_2 (c\alpha)_3 \cdots \right] \right] d\tau' \tag{50}$$

Now, P_k and P_ℓ are permutation operators. The result of the permutation includes every possible exchange of the coordinates of pairs of electrons. The effect of operators $\sum_k (-1)^k P_k$ and $\sum_\ell (-1)^\ell P_\ell$ will be unchanged if they are multiplied by another permutation operator, P. If P is chosen to be $(-1)^k P_k^{-1}$, then the first part of Eq. (50) becomes

$$\sum_k (-1)^k (-1)^k P_k P_k^{-1} \left[(a\alpha)_1 (b\alpha)_2 (c\beta)_3 \cdots (n\beta) \right] \tag{51}$$

But this is equal to

$$n!\left[(a\alpha)_1(b\alpha)_2(c\beta)_3 \cdots (n\beta)_n\right] \tag{52}$$

since there are n! indentical terms in the summation.

Operating on all of Eq. (50) will yield

$$H_{ij} = \int\left[(a\alpha)_1(b\alpha)_2(c\beta)_3 \cdots\right] H \sum_m (-1)^m P_m \left[(a\alpha)_1(b\beta)_2(c\alpha)_3 \cdots\right] d\tau' \tag{53}$$

Consider, H', one of the n! terms in H_{ij}.

$$H' = -\int\left[(a\alpha)_1(b\alpha)_2(c\beta)_3 \cdots\right] H \left[(a\alpha)_2(b\beta)_1(c\alpha)_3 \cdots\right] d\tau' \tag{54}$$

where there has been only one permutation of electron coordinates, 1 and 2, so that the sign is negative. If the orbital and spin functions are separated, then

$$H' = -\int(a_1b_2c_3 \cdots)H(a_2b_1c_3 \cdots)d\tau \int\alpha_1\beta_1 dw_1 \int\alpha_2^2 dw_2 \cdots \tag{55}$$

It is apparent that H' is zero because of the orthogonal spin functions. Indeed, all the n! terms of Eq. (53) analogous to H' will be zero except those terms for which the spins match identically. In practice, such terms are easily picked out of a spin state table.

The above discussion may be applied to one of the possible integrals, H_{12}, in the four electron problem.

$$H_{12} = \int t_1^* H\, t_2\, d\tau'$$

$$= \int \sum_k (-1)^k P_k (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 H \sum_\ell (-1)^\ell P_\ell (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 d\tau'$$

$$= - \int (a_1 b_2 c_3 d_4) H (a_1 b_3 c_2 d_4) d\tau$$

$$+ \int (a_1 b_2 c_3 d_4) H (a_1 b_3 c_4 d_2) d\tau \qquad (56)$$

$$+ \int (a_1 b_2 c_3 d_4) H (a_3 b_1 c_2 d_4) d\tau$$

$$- \int (a_1 b_2 c_3 d_4) H (a_3 b_1 c_4 d_2) d\tau$$

The four resulting terms may be abbreviated as

$$H_{12} = - (abcd) H (acbd) + (abcd) H (adbc) + (abcd) H (bcad) - (abcd) H (bdac) \qquad (57)$$

The first term involves a change in electron coordinates between the b and c orbitals. It is called the single exchange integral[31], bc. The other terms involve the respective permutations: bc and cd; ac and bc; and ac, bc, and cd. These three terms are called multiple exchange integrals. The exchange integrals have a plus or minus sign according to whether an even or odd number of permutations is involved.

To the approximation considered here, terms involving multiple exchange integrals will be dropped. The integral is thus shortened

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[31] Eyring, Walter, and Kimball, op. cit., p. 241.

to

$$H_{12} = - (abcd)H(acbd) = - bc \qquad (58)$$

This result has been generalized by Eyring in his first rule[32]:

> "The matrix element H_{ij} between two different t functions is zero unless the functions differ only in the spins of two orbitals, then it is the negative of the corresponding exchange integral."

This entire discussion may be repeated for the integral H_{ii}. An example of an integral of this form in the four electron problem is

$$H_{11} = \int t_1^* H t_1 \, d\tau$$

$$= \int \sum_k (-1)^k P \, (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 H \sum_k (-1)^k P_k (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 \, d$$

$$= (abcd)H(abcd) - (abcd)H(bacd) - (abcd)H(abdc)$$

$$= Q - ab - cd \qquad (59)$$

This result is generalized in Eyring's second rule:

> "The matrix element H_{ii} between a spin state function and itself is the coulombic integral, Q, minus the sum of all exchange integrals between orbitals having the same spin."

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[32] Eyring, Walter, and Kimball, op. cit., p. 241.

Transfer Integrals

The spin state theory which is developed for the valence bond approximation does not allow electron transfer; that is, the migration of an electron from one orbital to another. This is probably the most violent approximation in the valence bond approach. Because the method developed in this thesis does not specifically pair electrons in valence bonds, transfer states may be included by introducing additional spin states.

Consider the four electron case. The initial spin state distribution is given by the spin state table

	a	b	c	d
t_1	α	α	β	β
t_2	α	β	α	β
t_3	β	α	α	β
t_4	α	β	β	α
t_5	β	α	β	α
t_6	β	β	α	α

When discussing electron transfer, each spin is associated with the electron initially in the given orbitals, rather than with the orbital itself.

If an electron migrates from orbital c to orbital b, then spin

states t_3 and t_4 will not contribute to a description of the system because like spins cannot appear in the b orbital. Also, interchanging spins of the two electrons in orbital b must result in a change of sign; therefore, one may write

$$t_3' = t_4' = 0$$

$$t_2' = - t_1' \qquad (60)$$

$$t_6' = - t_5'$$

Once one has acquired the eigenfunctions which described the stable state of the system, as developed in an earlier part of this thesis, one may apply these conditions, Eq. (60), to obtain the functions describing the electron transfer states. An electron transfer function will belong to the same irreducible representation as the function from which it was derived; it may also be tested to establish its eigenvalue for S^2. Those functions having zero eigenvalue for S^2 will mix with the ordinary spin state eigenfunctions of S^2 to better describe the ground state.

Application of the Spin State Theory

The first problem to be considered, that of the square, is considered with some discussion. Thereafter, each problem is considered as briefly as possible.

Some eigenfunctions are set apart by an asterisk. These are functions which were obtained by symmetry arguments in order to obtain the function having the proper nodal surface. It is observed that such functions form simple linear combinations that are eigenfunctions of S^2.

The symbol Q is used to represent the Coulombic energy; and the symbols γ, δ, ϵ, etc., are used to depict nearest neighbor, next to nearest neighbor, etc. single exchange energies.

Four Electron Problem, C_{4v} Symmetry

Consider a square molecule belonging to the C_{4v} group. A spin state table for a four electron system with $S_z = 0$ is

	a	b	c	d
t_1	α	α	β	β
t_2	α	β	α	β
t_3	β	α	α	β
t_4	α	β	β	α
t_5	β	α	β	α
t_6	β	β	α	α

Using a square model, six spin state configurations may be constructed by applying each spin state eigenfunction to the model. These are given in Figure 3.

The C_{4v} character table is

	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	1	-1	1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0
Γ_1	4	0	0	2	0
Γ_2	2	2	0	0	2

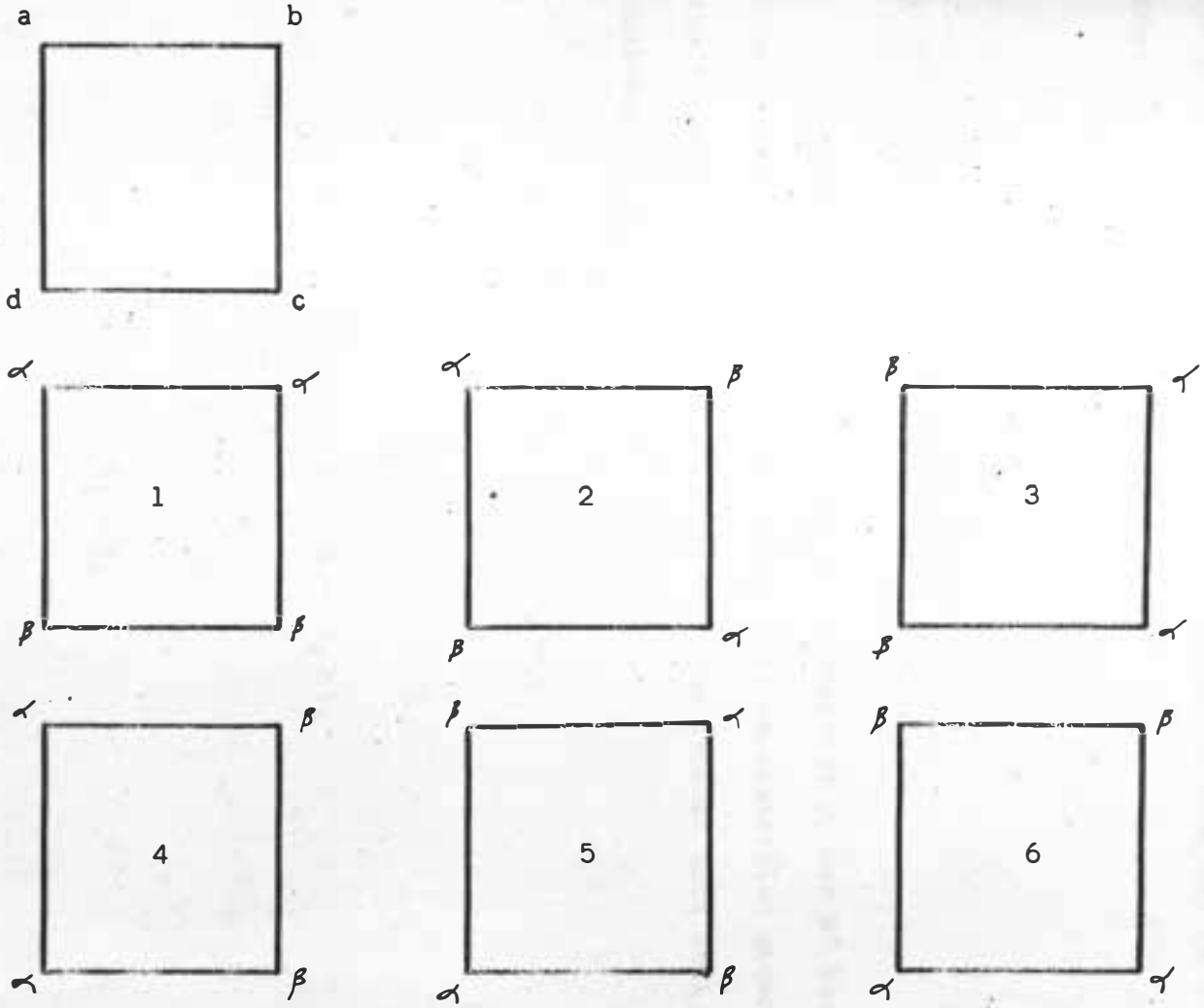

Figure 3. Application of spin state functions to a square model.

The six spin state functions serve as a basis for the reducible representations, Γ_1 and Γ_2. Functions t_1, t_3, t_4 and t_6 are partner functions for representation Γ_1, while t_2 and t_5 are partner functions for representation Γ_2. The reducible representations may be broken down by use of the character table.

$$\Gamma_1 = A_1 + B_1 + E$$
$$\Gamma_2 = A_1 + B_2 + E \tag{61}$$

Symmetry eigenfunctions may be constructed by use of the group theoretical generating machine. These will be classified according to their respective irreducible representations because such sets are noninteracting.

$$\begin{aligned}
&A_1 && \psi_1 = t_1 + t_3 + t_4 + t_6 \\
&A_1 && \psi_2 = t_2 + t_5 \\
&B_1 && \psi_3 = t_1 - t_3 - t_4 + t_6 \\
&B_2 && \psi_4 = t_2 - t_5 \\
&E && \psi_5 = t_1 - t_6 \\
&E && \psi_6 = t_3 - t_4
\end{aligned} \tag{62}$$

These functions are now tested to see if they are eigenfunctions of S^2. The effect of S^2 on each spin state function is given in

Table 4. Each row, $S^2 t_i$, in this table represents the linear combination of spin states given by Eq. (27). Each coefficient in the table is associated with the spin state which heads its column. Functions t_1 and t_2 are found to be the only functions not having an eigenvalue for S^2. These two functions are combined so that they are orthogonal in spin state space. The new functions, all of which are eigenfunctions of S^2, are

Representation		S^2
A_1	$\Psi_1' = \Psi_1 + 2\Psi_2 = t_1 + 2t_2 + t_3 + t_4 + 2t_5 + t_6$	2
A_1	$\Psi_2' = \Psi_1 - 2\Psi_2 = t_1 - 2t_2 + t_3 + t_4 - 2t_5 + t_6$	0
B_1	$\Psi_3' = \Psi_3 = t_1 - t_3 - t_4 + t_6$	0
B_2	$\Psi_4' = \Psi_4 = t_2 - t_5$	1
E	$\Psi_5' = \Psi_5 = t_1 - t_6$	1
E	$\Psi_6' = \Psi_6 = t_3 - t_4$	1

(63)

Now, the ground state energy might be found with either Ψ_2' or Ψ_3' because the eigenvalue of S^2 is zero for these functions. However, there is no interaction between the functions because Ψ_2' belongs to the A_1 irreducible representation and Ψ_3' belongs to the B_1 irreducible representation.

Solving the two one-by-one determinants, $\det|H_{22} - S_{22}E| = 0$ and $\det|H_{33} - S_{33}E| = 0$, yields

$$\begin{aligned} A_1 \quad & E_1 = Q + 2(\gamma - \delta) \\ B_1 \quad & E_2 = Q - 2(\gamma - \delta) \end{aligned} \tag{64}$$

Table 4. The effect of S^2 on each of the six spin state functions of the four electron problem

	t_1	t_2	t_3	t_4	t_5	t_6
S^2t_1	2	1	1	1	1	0
S^2t_2	1	2	1	1	0	1
S^2t_3	1	1	2	0	1	1
S^2t_4	1	1	0	2	1	1
S^2t_5	1	0	1	1	2	1
S^2t_6	0	1	1	1	1	2

Four Electron Problem, C_{3v} Symmetry

Consider a tetrahedral molecule which belongs to the C_{3v} group if only partial symmetry is considered.

The spin state table is the same as that listed in the previous four-electron problem. Using a tetrahedral model, the six spin state configurations are constructed and listed in Figure 4.

The C_{3v} character table is

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ_1	3	0	1
Γ_2	3	0	1

Partner basis functions for the reducible representations are:

$$\Gamma_1 : t_1, t_2, t_3$$
$$\Gamma_2 : t_4, t_5, t_6 \qquad (65)$$

Reducible representation breakdown:

$$\Gamma_1 = A_1 + E$$
$$\Gamma_2 = A_1 + E \qquad (66)$$

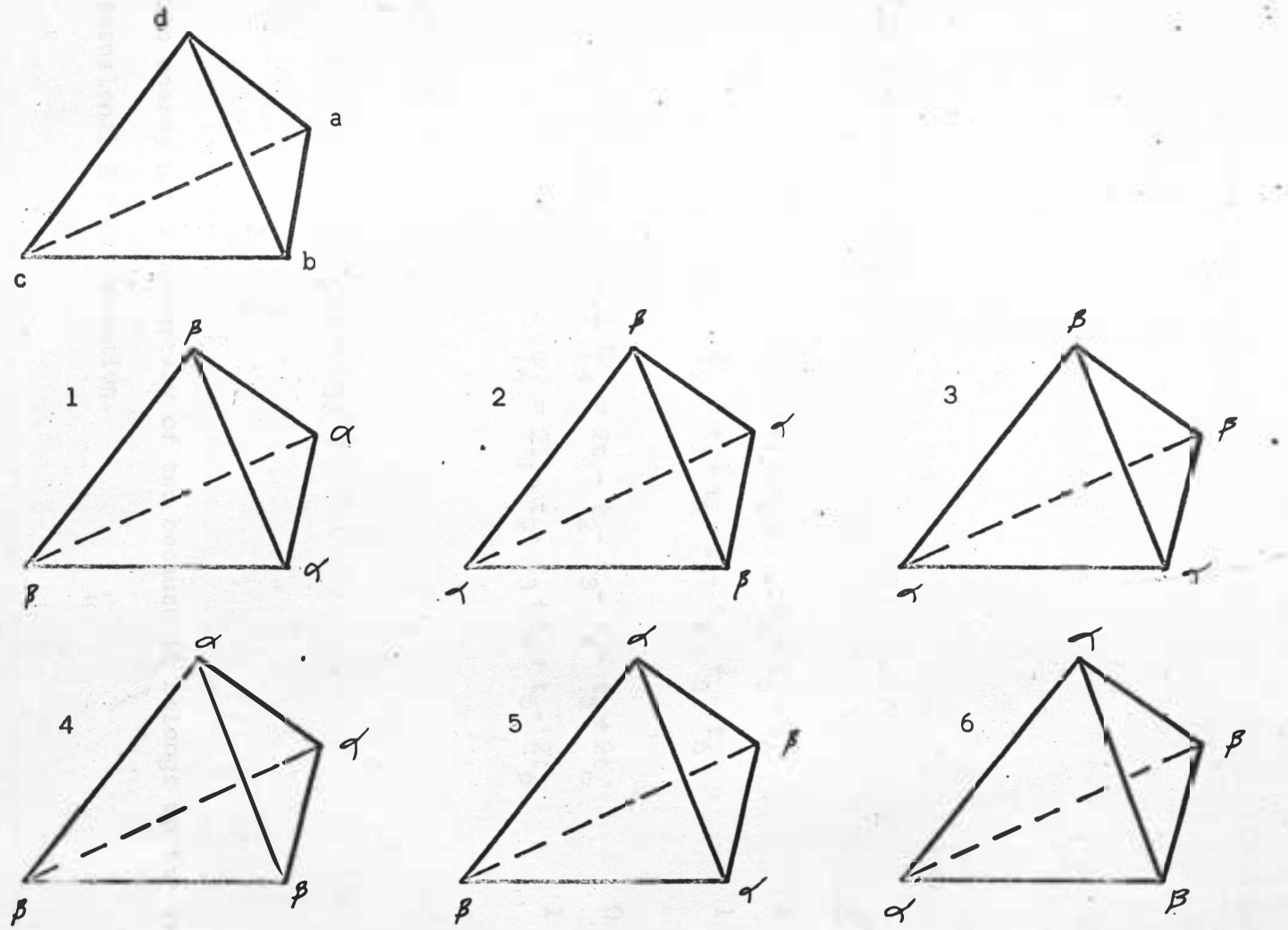

Figure 4. Application of spin state functions to a tetrahedral model.

Symmetry eigenfunctions

$$
\begin{aligned}
&A_1 \quad \psi_1 = t_1 + t_2 + t_3 \\
&A_1 \quad \psi_2 = t_4 + t_5 + t_6 \\
&\\
&E \quad \psi_3 = 2t_1 - t_2 - t_3 \\
*\ &E \quad \psi_4 = 2t_6 - t_5 - t_4
\end{aligned}
\tag{67}
$$

Eigenfunctions of S^2

		S^2
A_1	$\psi_1' = \psi_1 + \psi_2 = t_1 + t_2 + t_3 + t_4 + t_5 + t_6$	2
A_1	$\psi_2' = \psi_1 - \psi_2 = t_1 + t_2 + t_3 - t_4 - t_5 - t_6$	1
E	$\psi_3' = \psi_3 + \psi_4 = 2t_1 - t_2 - t_3 - t_4 - t_5 + 2t_6$	0
E	$\psi_4' = \psi_3 - \psi_4 = 2t_1 - t_2 - t_3 + t_4 + t_5 - 2t_6$	1

(68)

Ground state energy

$$
\text{Solving} \qquad \det \left| H_{33} - S_{33} E \right| = 0
$$

$$
E_1 = Q \tag{69}
$$

This energy has a degeneracy of two because it belongs to the two dimensional E representation.

Six Electron Problem, C_{6v} Symmetry

Consider a hexagonal molecule belonging to the C_{6v} group. A spin state table for a six electron system is given in Table 5. The spin state functions are superimposed on the hexagonal model in Figure 5 to yield twenty spin state configurations.

The C_{6v} character table is

	E	C	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	-1	1
B_2	1	-1	1	-1	1	-1
E_1	2	-2	-1	1	0	0
E_2	2	2	-1	-1	0	0
Γ_1	6	0	0	0	2	0
Γ_2	12	0	0	0	0	0
Γ_3	2	0	2	0	2	0

Partner basis functions for the reducible representations are:

$$\Gamma_1 : t_1, t_4, t_{10}, t_{11}, t_{17}, t_{20}$$

$$\Gamma_2 : t_2, t_3\ t_5\ t_7\ t_8, t_9\ t_{12}, t_{13}, t_{14}, t_{16}, t_{18}, t_{19} \qquad (70)$$

$$\Gamma_3 : t_6, t_{15}$$

Table 5. A Spin State Table for Six Electrons

	a	b	c	d	e	f
1	α	α	α	β	β	β
2	α	α	β	α	β	β
3	α	α	β	β	α	β
4	α	α	β	β	β	α
5	α	β	α	α	β	β
6	α	β	α	β	α	β
7	α	β	α	β	β	α
8	α	β	β	α	α	β
9	α	β	β	α	β	α
10	α	β	β	β	α	α
11	β	α	α	α	β	β
12	β	α	α	β	α	β
13	β	α	α	β	β	α
14	β	α	β	α	α	β
15	β	α	β	α	β	α
16	β	α	β	β	α	α
17	β	β	α	α	α	β
18	β	β	α	α	β	α
19	β	β	α	β	α	α
20	β	β	β	α	α	α

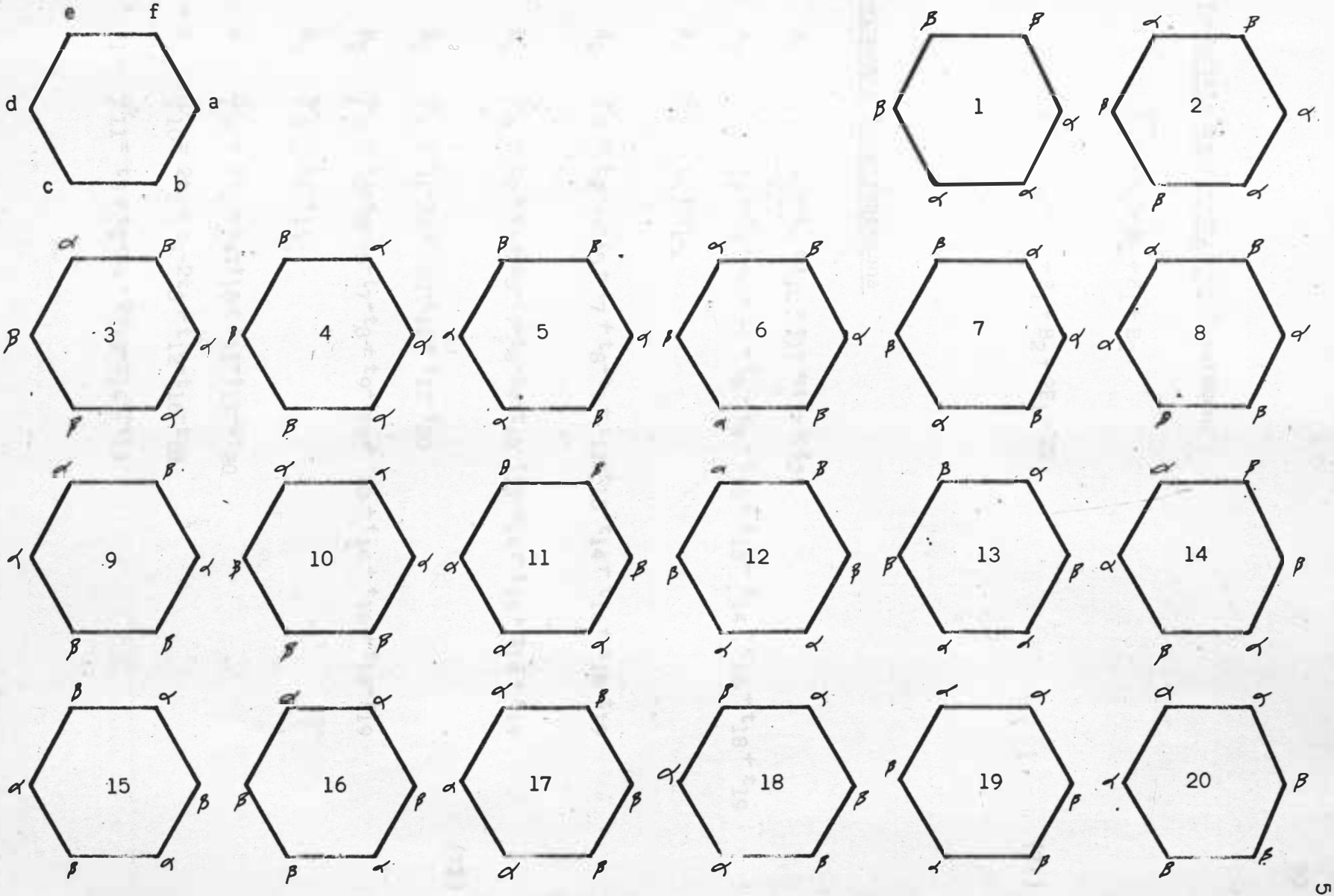

Figure 5. Application of spin state functions to a hexagonal model.

Reducible representation breakdown:

$$\Gamma_1 = A_1 + B_2 + E_1 + E_2$$

$$\Gamma_2 = A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2 \qquad (71)$$

$$\Gamma_3 = A_1 + B_2$$

Symmetry Eigenfunctions

$$A_1 \quad \psi_1 = t_1 + t_4 + t_{10} + t_{11} + t_{17} + t_{20}$$

$$A_1 \quad \psi_2 = t_2 + t_3 + t_5 + t_7 + t_8 + t_9 + t_{12} + t_{13} + t_{14} + t_{16} + t_{18} + t_{19}$$

$$A_1 \quad \psi_3 = t_6 + t_{15}$$

$$A_2 \quad \psi_4 = t_2 - t_3 - t_5 + t_7 + t_8 - t_9 + t_{12} - t_{13} - t_{14} + t_{16} + t_{18} - t_{19}$$

$$B_1 \quad \psi_5 = t_2 + t_3 + t_5 - t_7 - t_8 - t_9 - t_{12} - t_{13} - t_{14} + t_{16} + t_{18} + t_{19} \qquad (72)$$

$$B_2 \quad \psi_6 = t_1 - t_4 + t_{10} - t_{11} + t_{17} - t_{20}$$

$$B_2 \quad \psi_7 = t_2 - t_3 - t_5 - t_7 - t_8 + t_9 - t_{12} + t_{13} + t_{14} + t_{16} + t_{18} - t_{19}$$

$$B_2 \quad \psi_8 = t_6 - t_{15}$$

$$E_1 \quad \psi_9 = 2t_1 + t_4 - t_{10} + t_{11} - t_{17} - 2t_{20}$$

$$* \; E_1 \quad \psi_{10} = 2t_2 + t_7 - 2t_8 + t_{12} - t_{16} - t_{18}$$

$$* \; E_1 \quad \psi_{11} = t_3 + t_5 - t_9 + 2t_{13} - t_{14} - 2t_{19}$$

$E_2 \quad \psi_{12} = 2t_1 - t_4 - t_{10} - t_{11} - t_{17} + 2t_{20}$

$* E_2 \quad \psi_{13} = 2t_2 - t_7 + 2t_8 - t_{12} - t_{16} - t_{18}$

$* E_2 \quad \psi_{14} = t_3 + t_5 + t_9 - 2t_{13} + t_{14} - 2t_{19}$

Eigenfunctions of S^2

Representation		S^2
A_1	$\psi'_1 = \psi_1 + \psi_2 + \psi_3$	3
A_1	$\psi'_2 = 3\psi_1 - 2\psi_2 + 3\psi_3$	1
A_1	$\psi'_3 = \psi_1 - 3\psi_3$	1
A_2	$\psi'_4 = \psi_4$	0
B_1	$\psi'_5 = \psi_5$	1
B_2	$\psi'_6 = \psi_6 + \psi_7 + \psi_8$	0
B_2	$\psi'_7 = \psi_6 - \psi_7 + 3\psi_8$	2
B_2	$\psi'_8 = 4\psi_6 - \psi_7 - 6\psi_8$	0
E_1	$\psi'_9 = 2\psi_9 + \psi_{10} + \psi_{11}$	2
E_1	$\psi'_{10} = \psi_9 - \psi_{10} - \psi_{11}$	0
E_1	$\psi'_{11} = \psi_{10} + \psi_{11}$	1
E_2	$\psi'_{12} = \psi_{12} + \psi_{13} - \psi_{14}$	1
E_2	$\psi'_{13} = 2\psi_{12} - \psi_{13} + \psi_{14}$	1
E_2	$\psi'_{14} = \psi_{13} + \psi_{14}$	2

(73)

Zero - S^2 state energies

$$\begin{aligned} A_2 \qquad & E_1 = Q - 4\gamma - 4\delta - 3\epsilon \\ B_2 \qquad & E_2 = Q + (\sqrt{13} - 1)\gamma \\ B_2 \qquad & E_3 = Q - (\sqrt{13} + 1)\gamma \\ E \qquad & E_4 = Q - 2\gamma - \delta \end{aligned} \tag{74}$$

In the B_2 representation, the energies were obtained by dropping the δ and ϵ terms in the resulting quadratic equation.

Table 6. The Effect of S^2 on each of the Twenty Spin State Functions of the Six Electron Problem

	t_1	t_2	t_3	t_4	t_5	t_6	t_7	t_8	t_9	t_{10}	t_{11}	t_{12}	t_{13}	t_{14}	t_{15}	t_{16}	t_{17}	t_{18}	t_{19}	t_{20}
S^2t_1	3	1	1	1	1	1	1	0	0	0	1	1	1	0	0	0	0	0	0	0
S^2t_2	1	3	1	1	1	0	0	1	1	0	1	0	0	1	1	0	0	0	0	0
S^2t_3	1	1	3	1	0	1	0	1	0	0	0	1	0	1	0	1	0	0	0	0
S^2t_4	1	1	1	3	0	0	1	0	1	1	0	0	1	0	1	1	0	0	0	0
S^2t_5	1	1	0	0	3	1	1	1	1	0	1	0	0	0	0	0	1	1	0	0
S^2t_6	1	0	1	0	1	3	1	1	0	1	0	1	0	0	0	0	1	0	1	0
S^2t_7	1	0	0	1	1	1	3	0	1	1	0	0	1	0	0	0	0	1	1	0
S^2t_8	0	1	1	0	1	1	0	3	1	1	0	0	0	1	0	0	1	0	0	1
S^2t_9	0	1	0	1	1	0	1	1	3	1	0	0	0	0	1	0	0	1	0	1
S^2t_{10}	0	0	1	1	0	1	1	1	1	3	0	0	0	0	0	1	0	0	1	1
S^2t_{11}	1	1	0	0	1	0	0	0	0	0	3	1	1	1	1	0	1	1	0	0
S^2t_{12}	1	0	1	0	0	1	0	0	0	0	1	3	1	1	0	1	1	0	1	0
S^2t_{13}	1	0	0	1	0	0	1	0	0	0	1	1	3	0	1	1	0	1	1	0
S^2t_{14}	0	1	1	0	0	0	0	1	0	0	1	1	0	3	1	1	1	0	0	1
S^2t_{15}	0	1	0	1	0	0	0	0	1	0	1	0	1	1	3	1	0	1	0	1
S^2t_{16}	0	0	1	1	0	0	0	0	0	1	0	1	1	1	1	3	0	0	1	1
S^2t_{17}	0	0	0	0	1	1	0	1	0	0	1	1	0	1	0	0	3	1	1	1
S^2t_{18}	0	0	0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	3	1	1
S^2t_{19}	0	0	0	0	0	1	1	0	0	1	0	1	1	0	0	1	1	1	3	1
S^2t_{20}	0	0	0	0	0	0	0	1	1	1	0	0	0	1	1	1	1	1	1	3

Table 7. Eigenfunctions of S^2 for the Six Electron Hexagonal Problem

$$\psi_1' = t_1+t_2+t_3+t_4+t_5+t_6+t_7+t_8+t_9+t_{10}+t_{11}+t_{12}+t_{13}+t_{14}+t_{15}+t_{16}+t_{17}+t_{18}+t_{19}+t_{20}$$

$$\psi_2' = 3t_1-2t_2-2t_3+3t_4-2t_5+3t_6-2t_7-2t_8-2t_9+3t_{10}+3t_{11}-2t_{12}-2t_{13}-2t_{14}+3t_{15}-2t_{16}+3t_{17}-2t_{18}-2t_{19}+3t_{20}$$

$$\psi_3' = t_1\ t_4-3t_6+t_{10}+t_{11}-3t_{15}+t_{17}+t_{20}$$

$$\psi_4' = t_2-t_3-t_5+t_7+t_8-t_9+t_{12}-t_{13}-t_{14}+t_{16}+t_{18}-t_{19}$$

$$\psi_5' = t_2+t_3+t_5-t_7-t_8-t_9-t_{12}-t_{13}-t_{14}+t_{16}+t_{18}+t_{19}$$

$$\psi_6' = t_1-t_2+t_3-t_4+t_5+3t_6+t_7+t_8-t_9+t_{10}-t_{11}+t_{12}-t_{13}-t_{14}-3t_{15}-t_{16}+t_{17}-t_{18}+t_{19}-t_{20}$$

$$\psi_7' = t_1+t_2-t_3-t_4-t_5+t_6-t_7-t_8+t_9+t_{10}-t_{11}-t_{12}+t_{13}+t_{14}-t_{15}+t_{16}+t_{17}+t_{18}-t_{19}-t_{20}$$

$$\psi_8' = 4t_1-t_2+t_3-4t_4+t_5-6t_6+t_7+t_8-t_9+4t_{10}-4t_{11}+t_{12}-t_{13}-t_{14}+6t_{15}-t_{16}+4t_{17}-t_{18}+t_{19}-4t_{20}$$

$$\psi_9' = 4t_1+2t_2+t_3+2t_4+t_5+t_7-2t_8-t_9-2t_{10}+2t_{11}+t_{12}+2t_{13}-t_{14}-t_{16}-2t_{17}-t_{18}-2t_{19}-4t_{20}$$

$$\psi_{10}' = 2t_1-2t_2-t_3+t_4-t_5-t_7+2t_8+t_9-t_{10}+t_{11}-t_{12}-2t_{13}+t_{14}+t_{16}-t_{17}+t_{18}+2t_{19}-2t_{20}$$

$$\psi_{11}' = 2t_2-t_3-t_5+t_7-2t_8+t_9+t_{12}-2t_{13}+t_{14}-t_{16}-t_{18}+2t_{19}$$

$$\psi_{13}' = 2t_1+2t_2-t_3-t_4-t_5-t_7+2t_8-t_9-t_{10}-t_{11}-t_{12}+2t_{13}-t_{14}-t_{16}-t_{17}-t_{18}+2t_{19}+2t_{20}$$

$$\psi_{14}' = 4t_1-2t_2+t_3-2t_4+t_5+t_7-2t_8+t_9-2t_{10}-2t_{11}+t_{12}-2t_{13}+t_{14}+t_{16}-2t_{17}+t_{18}-2t_{19}+4t_{20}$$

$$\psi_{15}' = 2t_2+t_3+t_5-t_7+2t_8+t_9-t_{12}-2t_{13}+t_{14}-t_{16}-t_{18}-2t_{19}$$

Six Electron Problem, O Symmetry

Consider an octahedral molecule belonging to the O symmetry group. The spin state table is the same as that used in the hexagonal case and is given by Table 5. Using the octahedral model, twenty spin state configurations are constructed. These are given in Figure 6.

The O character table is:

	E	$8C_3$	$3C_2$	$6C_4$	$6C_4^2$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1
Γ_1	8	2	0	0	0
Γ_2	12	0	4	0	0

Partner functions for the reduced representations are:

$$\Gamma_1: t_1, t_4, t_6, t_{10}, t_{11}, t_{15}, t_{17}, t_{20} \qquad (75)$$

$$\Gamma_2: t_2, t_3, t_5, t_7, t_8, t_9, t_{12}, t_{13}, t_{14}, t_{16}, t_{18}, t_{19}$$

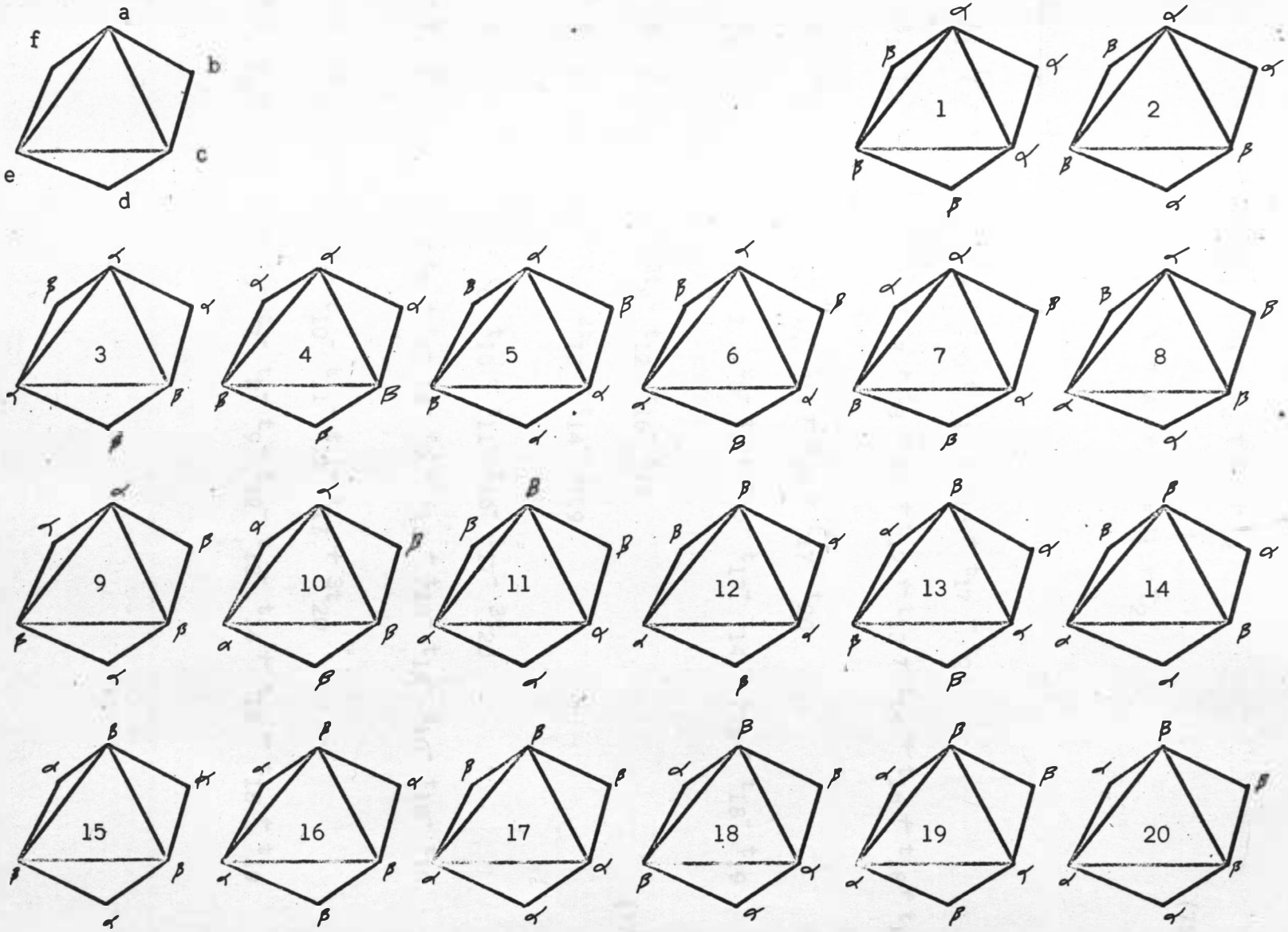

Figure 6. Application of spin state functions to an octahedral model.

Reducible representation breakdown:

$$\Gamma_1 = A_1 + A_2 + T_1 + T_2$$

$$\Gamma_2 = A_1 + A_2 + 2E + T_1 + T_2 \qquad (76)$$

Symmetry eigenfunctions

$$A_1 \quad \psi_1 = t_1 + t_4 + t_6 + t_{10} + t_{11} + t_{15} + t_{17} + t_{20}$$

$$A_1 \quad \psi_2 = t_2 + t_3 + t_5 + t_7 + t_8 + t_9 + t_{12} + t_{13} + t_{14} + t_{16} + t_{18} + t_{19}$$

$$A_2 \quad \psi_3 = t_1 - t_4 - t_6 + t_{10} - t_{11} + t_{15} + t_{17} - t_{20}$$

$$A_2 \quad \psi_4 = t_2 - t_3 - t_5 + t_7 + t_8 - t_9 + t_{12} - t_{13} - t_{14} + t_{16} + t_{18} - t_{19}$$

$$E \quad \psi_5 = 2t_2 - t_7 + 2t_8 - t_{12} - t_{16} - t_{18} \qquad (77)$$

$$* E \quad \psi_6 = t_3 + t_5 + t_9 - 2t_{13} + t_{14} - 2t_{19}$$

$$T_1 \quad \psi_7 = 3t_1 + t_4 + t_6 - t_{10} + t_{11} - t_{15} - t_{17} - 3t_{20}$$

$$* T_1 \quad \psi_8 = t_2 + t_3 + t_5 + t_7 - t_8 - t_9 + t_{12} + t_{13} - t_{14} - t_{16} - t_{18} - t_{19}$$

$$T_2 \quad \psi_9 = 3t_1 - t_4 - t_6 - t_{10} - t_{11} - t_{15} - t_{17} + 3t_{20}$$

$$* T_2 \quad \psi_{10} = t_2 + t_3 + t_5 - t_7 - t_8 - t_9 - t_{12} - t_{13} - t_{14} + t_{16} + t_{18} + t_{19}$$

Eigenfunctions of S^2 | S^2

$$
\begin{array}{lll}
A_1 & \psi_1' = \psi_1 + \psi_2 & 3 \\
A_1 & \psi_2' = 3\psi_1 - 2\psi_2 & 1 \\
A_2 & \psi_3' = \psi_3 + \psi_4 & 0 \\
A_2 & \psi_4' = 3\psi_3 - 2\psi_4 & 0 \\
E & \psi_5' = \psi_5 + \psi_6 & 2 \\
E & \psi_6' = \psi_5 - \psi_6 & 1 \\
T_1 & \psi_7' = \psi_7 + \psi_8 & 2 \\
T_1 & \psi_8' = \psi_7 - 2\psi_8 & 0 \\
T_2 & \psi_9' = \psi_9 + \psi_{10} & 1 \\
T_2 & \psi_{10}' = \psi_9 - 2\psi_{10} & 1
\end{array}
\qquad (78)
$$

These are expanded in terms of spin state functions in Table 8.

Zero - S^2 state energies

$$
\begin{array}{ll}
A_2 & E_1 = Q - 3\delta \\
A_2 & E_2 = Q - 6\gamma + 3\delta \\
T_1 & E_3 = Q - 2\gamma - \delta
\end{array}
\qquad (79)
$$

Table 8. Eigenfunctions of S^2 for the Six Electron Octahedral Problem

$$\psi_1' = t_1+t_2+t_3+t_4+t_5+t_6+t_7+t_8+t_9+t_{10}+t_{11}+t_{12}+t_{13}+t_{14}+t_{15}+t_{16}+t_{17}+t_{18}+t_{19}+t_{20}$$

$$\psi_2' = 3t_1-2t_2-2t_3+3t_4-2t_5+3t_6-2t_7-2t_8-2t_9+3t_{10}+3t_{11}-2t_{12}-2t_{13}-2t_{14}+3t_{15}-2t_{16}+3t_{17}-2t_{18}-2t_{19}+3t_{20}$$

$$\psi_3' = t_1+t_2-t_3-t_4-t_5-t_6+t_7+t_8-t_9\ t_{10}-t_{11}+t_{12}-t_{13}-t_{14}+t_{15}+t_{16}+t_{17}+t_{18}-t_{19}-t_{20}$$

$$\psi_4' = 3t_1-2t_2+2t_3-3t_4+2t_5-3t_6-2t_7-2t_8+2t_9+3t_{10}-3t_{11}-2t_{12}+2t_{13}+2t_{14}+3t_{15}-2t_{16}+3t_{17}-2t_{18}+2t_{19}-3t_{20}$$

$$\psi_5' = 2t_2+t_3+t_5-t_7+2t_8+t_9-t_{12}-2t_{13}+t_{14}-t_{16}-t_{18}-2t_{19}$$

$$\psi_6' = 2t_2-t_3-t_5-t_7+2t_8-t_9-t_{12}+2t_{13}-t_{14}-t_{16}-t_{18}+2t_{19}$$

$$\psi_7' = 3t_1+t_2+t_3+t_4+t_5+t_6+t_7-t_8-t_9-t_{10}+t_{11}+t_{12}+t_{13}-t_{14}-t_{15}-t_{16}-t_{17}-t_{18}-t_{19}-3t_{20}$$

$$\psi_8' = 3t_1-2t_2-2t_3+t_4-2t_5+t_6-2t_7+2t_8+2t_9-t_{10}+t_{11}-2t_{12}-2t_{13}+2t_{14}-t_{15}+2t_{16}-t_{17}+2t_{18}-2t_{19}-3t_{20}$$

$$\psi_9' = 3t_1+t_2+t_3-t_4+t_5-t_6-t_7-t_8-t_9-t_{10}-t_{11}-t_{12}-t_{13}-t_{14}-t_{15}+t_{16}-t_{17}+t_{18}+t_{19}+3t_{20}$$

$$\psi_{10}' = 3t_1-2t_2-2t_3-t_4-2t_5-t_6+2t_7+2t_8+2t_9-t_{10}-t_{11}+2t_{12}+2t_{13}+2t_{14}-t_{15}-2t_{16}-t_{17}-2t_{18}-2t_{19}+3t_{20}$$

Eight Electron Problem, O_h Symmetry

Consider a cubical molecule belonging to the O_h symmetry group. A spin state table for an eight electron system with $S_z = 0$ is given in Table 9. Using a model cube, the spin state functions may be applied to produce seventy spin state configurations. These are given in Figure 7.

The O_h character table is given in Figure 8.

The partner functions for the reducible representations are:

$$\Gamma_1: t_i,\ i = 1,3,8,10,12,15,19,24,26,28,29,35,36,42,43,45,47,52,56,59,61,63,68,70$$

$$\Gamma_2: t_j;\ j = 2,7,9,11,16,18,20,23,25,27,30,34,37,41,44,46,48,51,53,55,60,62,64,69$$

$$\Gamma_3: t_k;\ k = 4,14,22,32,39,49,57,67 \tag{80}$$

$$\Gamma_4: t_l;\ l = 5,13,33,38,58,68$$

$$\Gamma_5: t_m;\ m = 6,17,31,40,54,65$$

$$\Gamma_6: t_n;\ n = 21,50$$

Reducible representation breakdown:

$$\Gamma_1 = A_{1g} + A_{1u} + E_g + E_u + F_{1g} + F_{1u} + 2F_{2g} + 2F_{2u} \tag{81}$$

$$\Gamma_2 = A_{1g} + A_{2u} + E_g + E_u + F_{1g} + 2F_{1u} + 2F_{2g} + F_{2u}$$

Table 9. A Spin State Table for Eight Electrons

	a	b	c	d	e	f	g	h		a	b	c	d	e	f	g	h
1	α	α	α	α	β	β	β	β	36	β	α	α	α	α	β	β	β
2	α	α	α	β	α	β	β	β	37	β	α	α	α	β	α	β	β
3	α	α	α	β	β	α	β	β	38	β	α	α	α	β	β	α	β
4	α	α	α	β	β	β	α	β	39	β	α	α	α	β	β	β	α
5	α	α	α	β	β	β	β	α	40	β	α	α	β	α	α	β	β
6	α	α	β	α	α	β	β	β	41	β	α	α	β	α	β	α	β
7	α	α	β	α	β	α	β	β	42	β	α	α	β	α	β	β	α
8	α	α	β	α	β	β	α	β	43	β	α	α	β	β	α	α	β
9	α	α	β	α	β	β	β	α	44	β	α	α	β	β	α	β	α
10	α	α	β	β	α	α	β	β	45	β	α	α	β	β	β	α	α
11	α	α	β	β	α	β	α	β	46	β	α	β	α	α	α	β	β
12	α	α	β	β	α	β	β	α	47	β	α	β	α	α	β	α	β
13	α	α	β	β	β	α	α	β	48	β	α	β	α	α	β	β	α
14	α	α	β	β	β	α	β	α	49	β	α	β	α	β	α	α	β
15	α	α	β	β	β	β	α	α	50	β	α	β	α	β	α	β	α
16	α	β	α	α	α	β	β	β	51	β	α	β	α	β	β	α	α
17	α	β	α	α	β	α	β	β	52	β	α	β	β	α	α	α	β
18	α	β	α	α	β	β	α	β	53	β	α	β	β	α	α	β	α
19	α	β	α	α	β	β	β	α	54	β	α	β	β	α	β	α	α
20	α	β	α	β	α	α	β	β	55	β	α	β	β	β	α	α	α
21	α	β	α	β	α	β	α	β	56	β	β	α	α	α	α	β	β
22	α	β	α	β	α	β	β	α	57	β	β	α	α	α	β	α	β
23	α	β	α	β	β	α	α	β	58	β	β	α	α	α	β	β	α
24	α	β	α	β	β	α	β	α	59	β	β	α	α	β	α	α	β
25	α	β	α	β	β	β	α	α	60	β	β	α	α	β	α	β	α
26	α	β	β	α	α	α	β	β	61	β	β	α	α	β	β	α	α
27	α	β	β	α	α	β	α	β	62	β	β	α	β	α	α	α	β
28	α	β	β	α	α	β	β	α	63	β	β	α	β	α	α	β	α
29	α	β	β	α	β	α	α	β	64	β	β	α	β	α	β	α	α
30	α	β	β	α	β	α	β	α	65	β	β	α	β	β	α	α	α
31	α	β	β	α	β	β	α	α	66	β	β	β	α	α	α	α	β
32	α	β	β	β	α	α	α	β	67	β	β	β	α	α	α	β	α
33	α	β	β	β	α	α	β	α	68	β	β	β	α	α	β	α	α
34	α	β	β	β	α	β	α	α	69	β	β	β	α	β	α	α	α
35	α	β	β	β	β	α	α	α	70	β	β	β	β	α	α	α	α

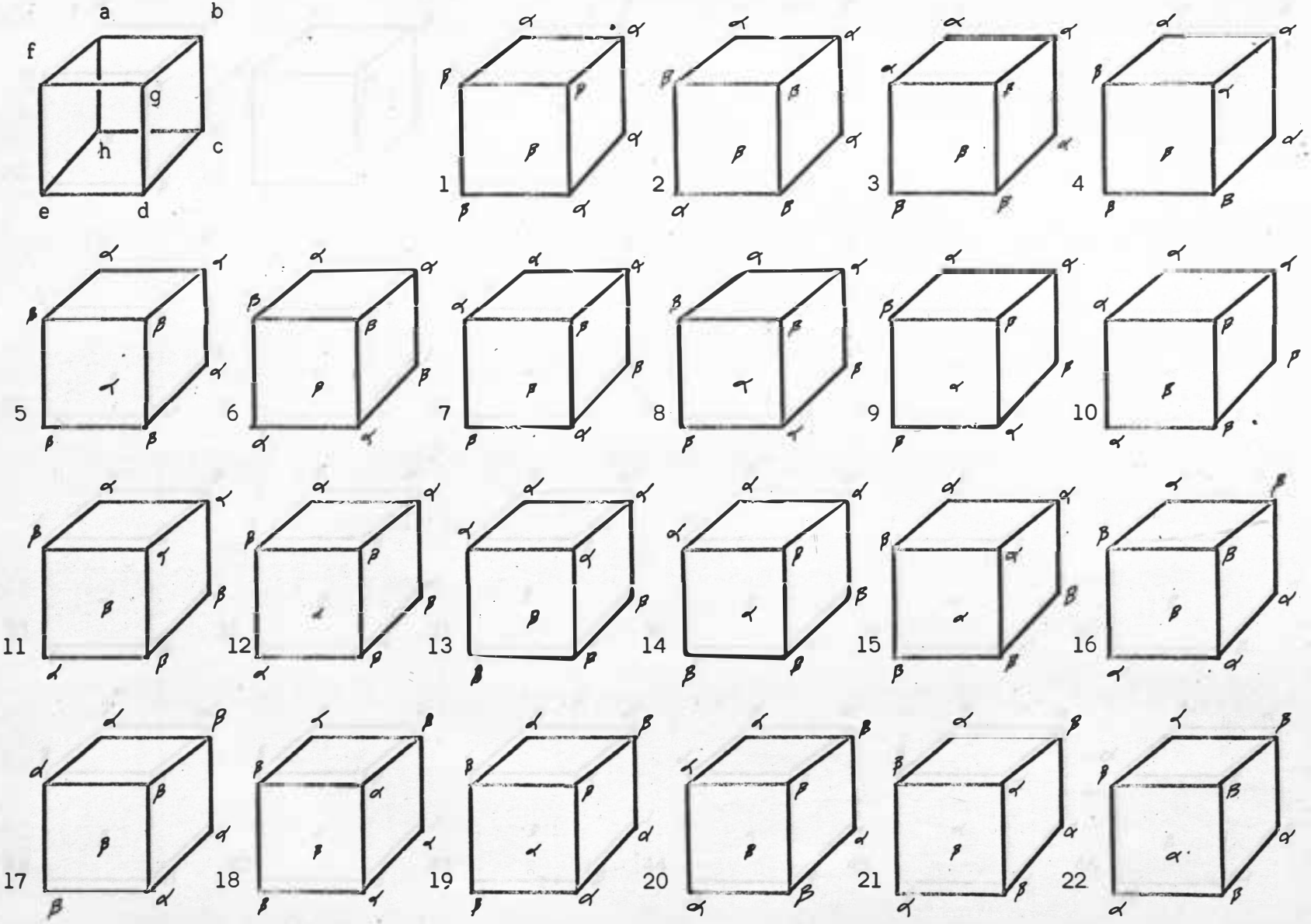

Figure 7. Application of spin state functions to a cubical model.

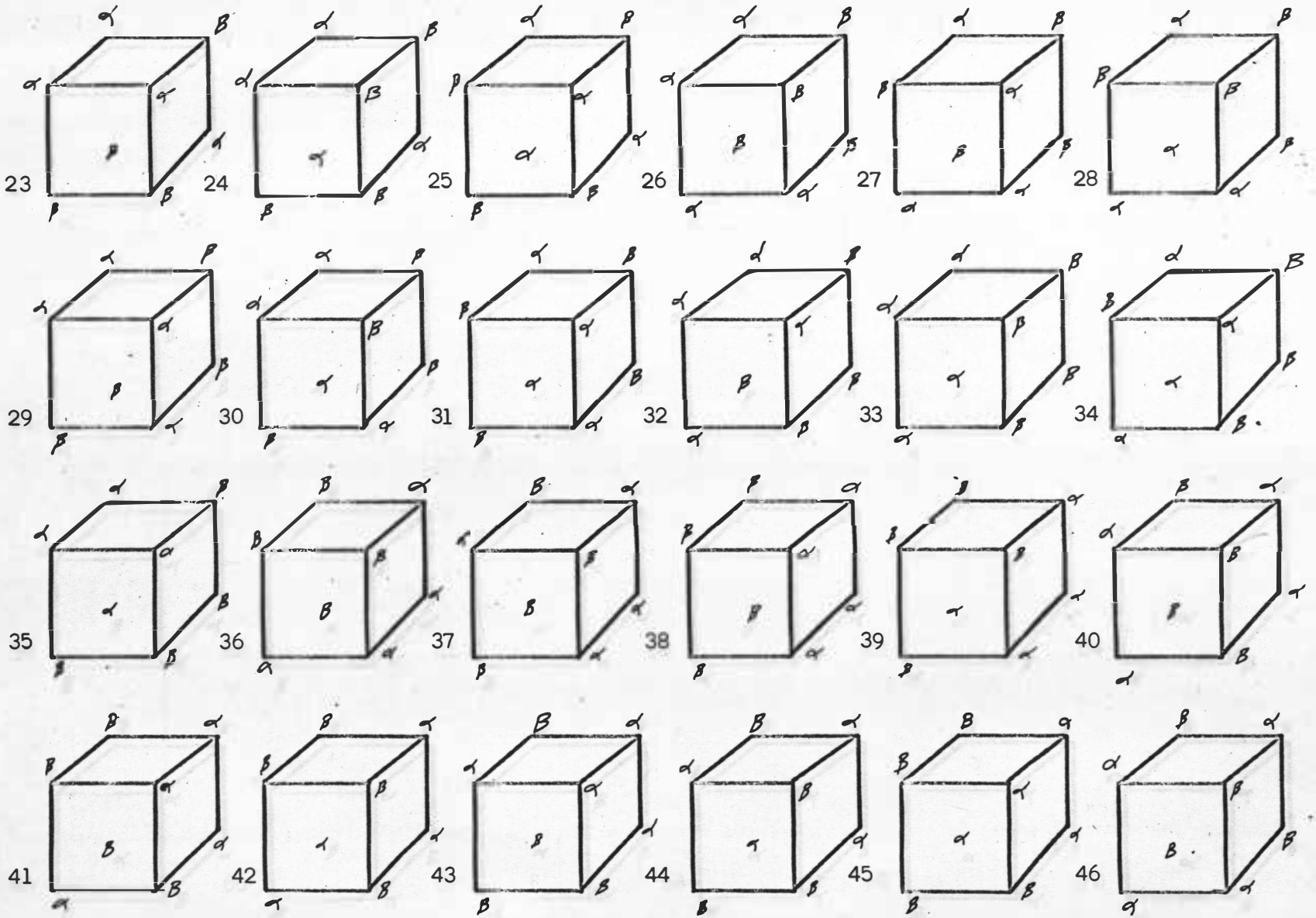

Figure 7. Continued.

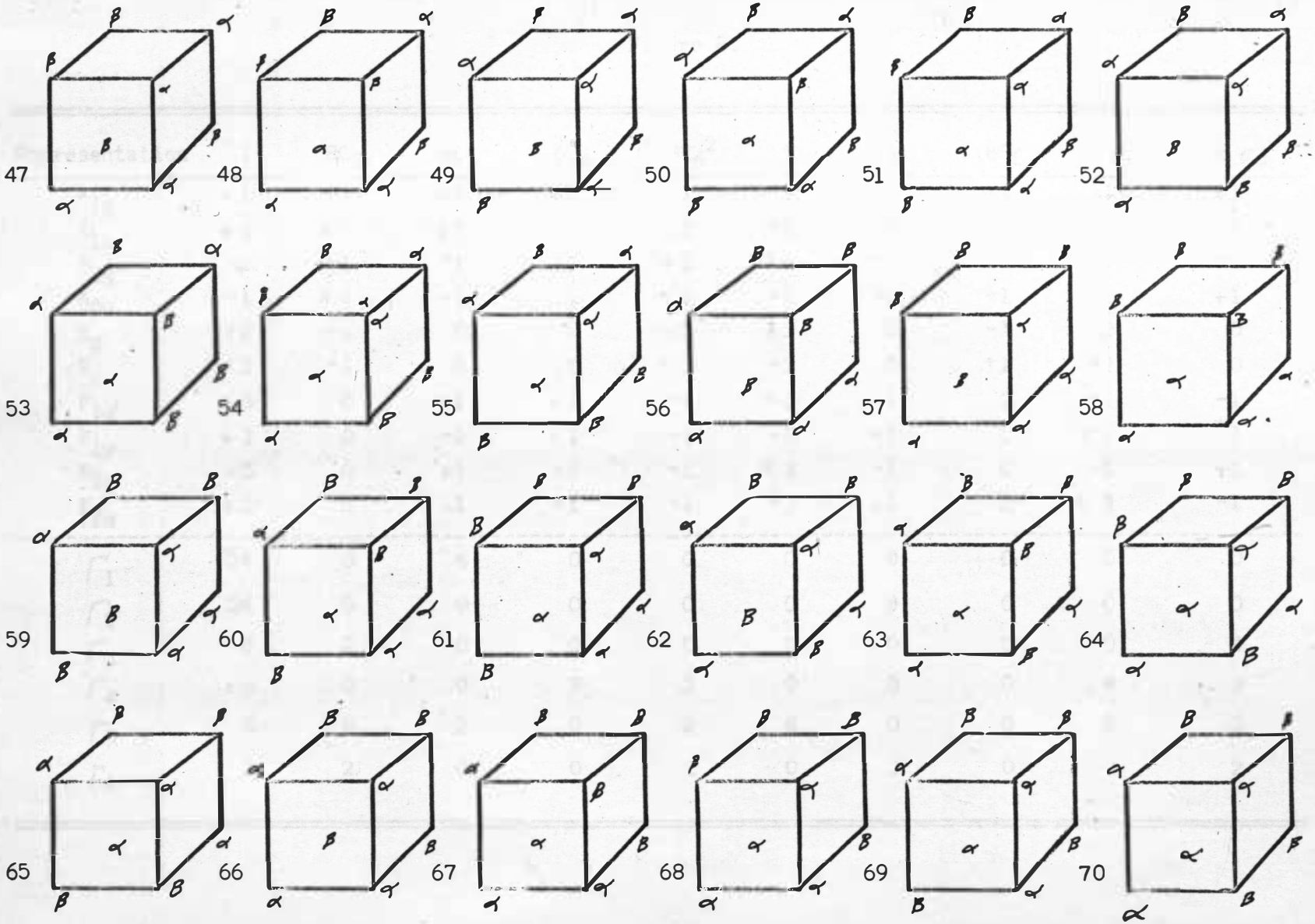

Figure 7. Continued.

Figure 8.

Representation	I	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0
E_u	+2	-1	0	0	+2	-2	0	+1	-2	0
F_{1g}	+3	0	-1	+1	-1	+3	+1	0	-1	-1
F_{1u}	+3	0	-1	+1	-1	-3	-1	0	+1	+1
F_{2g}	+3	0	+1	-1	-1	+3	-1	0	-1	+1
F_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1
Γ_1	24	0	4	0	0	0	0	0	0	0
Γ_2	24	0	0	0	0	0	0	0	0	0
Γ_3	8	2	0	0	0	0	0	0	0	4
Γ_4	6	0	0	2	2	0	0	0	4	2
Γ_5	6	0	2	0	2	6	0	0	2	2
Γ_6	2	2	0	0	2	0	2	0	0	2

$$\Gamma_3 = A_{1g} + A_{2u} + F_{1u} + F_{2g}$$

$$\Gamma_4 = A_{1g} + E_g + F_{1u}$$

$$\Gamma_5 = A_{1g} + E_g + F_{2g}$$

$$\Gamma_6 = A_{1g} + A_{2u}$$

Thus, the 70 by 70 secular determinant may be expressed as nine smaller determinants:

A_{1g}	(6 by 6)	F_{1g}	(2 by 2)	
A_{1u}	(1 by 1)	F_{1u}	(5 by 5)	
A_{2u}	(3 by 3)	F_{2g}	(6 by 6)	(82)
E_g	(4 by 4)	F_{2u}	(3 by 3)	
E_u	(2 by 2)			

The A representations are singly degenerate, the E representations doubly degenerate, and the F representations are triply degenerate. The symmetry eigenfunctions are given in Table 10.

Eigenfunctions of S^2

		S^2
A_{1g}	$\Psi_1 = \psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6$	4

$$A_{1g} \quad \psi_2' = \psi_1 + \psi_2 - 2\psi_3 - \psi_4 - 4\psi_5 - \psi_6 \qquad 0$$

$$A_{1g} \quad \psi_3' = \psi_1 + \psi_2 + 21\psi_3 - 24\psi_4 - 4\psi_5 - 24\psi_6 \qquad 0$$

$$A_{1g} \quad \psi_4' = \psi_1 - \psi_2 - \psi_4 + 3\psi_6 \qquad 0$$

$$A_{1g} \quad \psi_5' = \psi_1 + \psi_2 - 6\psi_3 - 6\psi_4 + 8\psi_5 - 6\psi_6 \qquad 2$$

$$A_{1g} \quad \psi_6' = \psi_1 - \psi_2 + 2\psi_4 - \psi_6 \qquad 2$$

$$A_{1u} \quad \psi_7' = \psi_7 \qquad 0$$

$$A_{2u} \quad \psi_8' = \psi_8 + \psi_9 2 + \psi_{10} \qquad 3$$

$$A_{2u} \quad \psi_9' = \psi_8 + \psi_9 - 8\psi_{10} \qquad 1 \qquad (83)$$

$$A_{2u} \quad \psi_{10}' = \psi_8 - 3\psi_9 \qquad 1$$

$$E_g \quad \psi_{11}' = \psi_{11} + \psi_{12} - 2\psi_{13} \qquad 0$$

$$E_g \quad \psi_{12}' = \psi_{11} - \psi_{12} - 2\psi_{14} \qquad 0$$

$$E_g \quad \psi_{13}' = \psi_{11} - \psi_{12} + 4\psi_{14} \qquad 2$$

$$E_g \quad \psi_{14}' = \psi_{11} + \psi_{12} + 4\psi_{13} \qquad 2$$

E_u $\quad \psi'_{15} = \psi_{15}$ $\quad$ 2

E_u $\quad \psi'_{16} = \psi_{16}$ $\quad$ 1

F_{1g} $\quad \psi'_{17} = \psi_{17}$ $\quad$ 1

F_{1g} $\quad \psi'_{18} = \psi_{18}$ $\quad$ 1

These terms are not expanded in terms of spin states because of their length. The F_{1u}, F_{2g} and F_{2u} representations are not listed.

Zero - S^2 state energies

$$A_{1g} \quad E_1 = Q - 2.5\gamma - 2.8\delta - 3.9\epsilon$$

$$A_{1g} \quad E_2 = Q - 4.5\gamma - 7.2\delta + 3.4\epsilon$$

$$A_{1g} \quad E_3 = Q + 0.5\gamma - 10.2\delta + \epsilon \qquad (84)$$

$$A_{1u} \quad E_4 = Q - 6\gamma - 2\epsilon$$

$$E_g \quad E_5 = Q - 5.7\gamma$$

$$E_g \quad E_5 = Q - 3.3\gamma$$

Table 10. Symmetry Eigenfunctions for Eight Electrons, O_h Symmetry

A_{1g} $\psi_1 = \sum_i t_i$

A_{1g} $\psi_2 = \sum_j t_j$

A_{1g} $\psi_3 = \sum_k t_k$

A_{1g} $\psi_4 = \sum_l t_l$

A_{1g} $\psi_5 = \sum_m t_m$

A_{1g} $\psi_6 = \sum_n t_n$

A_{1u} $\psi_7 = t_1 - t_3 - t_8 + t_{10} - t_{12} + t_{15} - t_{19} + t_{24} - t_{26} + t_{28} + t_{29} - t_{35} - t_{36} + t_{42} + t_{43} - t_{45} + t_{47} - t_{52} + t_{56}$
$- t_{59} \quad t_{61} - t_{63} - t_{68} \quad t_{70}$

A_{2u} $\psi_8 = t_2 - t_7 - t_9 + t_{11} + t_{16} + t_{18} + t_{20} + t_{23} + t_{25} + t_{27} - t_{30} + t_{34} - t_{37} + t_{41} - t_{44} - t_{46} - t_{48} - t_{51} - t_{53}$
$- t_{55} - t_{60} + t_{62} + t_{64} - t_{69}$

A_{2u} $\psi_9 = t_4 - t_{14} + t_{22} + t_{32} - t_{39} - t_{49} + t_{57} - t_{67}$

A_{2u} $\psi_{10} = t_{21} - t_{50}$

Table 10. Continued.

$$E_g \quad \psi_{11} = 2t_1 - t_3 - t_8 - t_{10} + 2t_{12} - t_{15} - t_{19} + 2t_{24} + 2t_{26} - t_{28} - t_{29} - t_{35} + \sum_{E_g} (Ct)_{71-i}$$

$$E_g \quad \psi_{12} = 2t_2 - t_7 + 2t_9 - t_{11} - t_{16} - t_{18} - t_{20} - t_{23} + 2t_{25} + 2t_{27} - t_{30} - t_{34} + \sum_{E_g} (Ct)_{71-j}$$

$$E_g \quad \psi_{13} = 2t_5 - t_{13} - t_{33} - t_{38} - t_{58} + 2t_{66}$$

$$E_g \quad \psi_{14} = 2t_6 - t_{17} - t_{31} - t_{40} - t_{54} + 2t_{65}$$

$$E_u \quad \psi_{15} = 2t_1 + t_3 + t_8 - t_{10} - 2t_{12} - t_{15} + t_{19} + 2t_{24} - 2t_{26} - t_{28} - t_{29} + t_{35} + \sum_{E_u} (Ct)_{71-i}$$

$$E_u \quad \psi_{16} = 2t_2 + t_7 - 2t_9 - t_{11} - t_{16} - t_{18} - t_{20} - t_{23} + 2t_{25} + 2t_{27} + t_{30} - t_{34} + \sum_{E_u} (Ct)_{71-j}$$

$$F_{1g} \quad \psi_{17} = 2t_1 - t_3 - t_8 - t_{10} + t_{15} - t_{19} + 2t_{26} - t_{28} - t_{29} + t_{35} - \sum_{F_{1g}} (Ct)_{71-i}$$

$$F_{1g} \quad \psi_{18} = 2t_2 - t_7 - t_{11} - t_{16} + t_{18} - t_{20} + t_{23} - 2t_{25} + t_{30} + t_{34} - \sum_{F_{1g}} (Ct)_{71-j}$$

$$F_{1u} \quad \psi_{19} = 2t_1 + t_3 + t_8 - t_{10} + t_{15} + t_{19} - 2t_{26} - t_{28} - t_{29} - t_{35} - \sum_{F_{1u}} (Ct)_{71-i}$$

Table 10. Continued.

$$F_{1u} \quad \psi_{20} = 4t_2 - t_7 + t_{11} + t_{16} - t_{18} + t_{20} - t_{23} - 2t_{27} + t_{30} - t_{34} - t_{37} + t_{41} + 2t_{44} - 4t_{46} - t_{48} + t_{51} - t_{53} + t_{55} + t_{60} - 2t_{62} - t_{64}$$

$$* F_{1u} \quad \psi_{21} = 4t_{69} - t_{64} + t_{60} + t_{55} - t_{53} + t_{51} - t_{48} - 2t_{44} + t_{41} - t_{37} - t_{34} + t_{30} + 2t_{27} - 4t_{25} - t_{23} + t_{20} - t_{18} + t_{16} + t_{11} - 2t_9 - t_7$$

$$F_{1u} \quad \psi_{22} = 3t_4 + t_{14} - t_{22} - t_{32} + t_{39} + t_{49} - t_{57} - 3t_{67}$$

$$F_{1u} \quad \psi_{23} = t_5 - t_{66}$$

$$F_{2g} \quad \psi_{24} = 4t_1 + t_3 + t_8 + t_{10} - 2t_{12} - t_{15} + t_{19} - 2t_{24} + 4t_{26} + t_{28} + t_{29} - t_{35} + t_{36} - t_{42} - t_{43} - 2t_{47} - t_{52} + t_{56} - 2t_{59} - t_{61} - t_{63} - t_{68}$$

$$* F_{2g} \quad \psi_{25} = 4t_{70} + t_{68} + t_{63} + t_{61} - 2t_{59} - t_{56} + t_{52} - 2t_{47} + 4t_{45} + t_{43} + t_{42} - t_{36} + t_{35} - t_{29} - t_{28} - 2t_{24} - t_{19} + t_{15} - 2t_{12} - t_{10} - t_8 - t_3$$

Table 10. Continued.

$$F_{2g}\ \psi_{26} = 4t_2 + t_7 - 2t_9 + t_{11} + t_{16} - t_{18} + t_{20} - t_{23} - 2t_{27} - t_{30} - t_{34} + t_{41} - 2t_{44} + 4t_{46} + t_{48} - t_{51} + t_{53} - t_{55} - t_{60} - 2t_{62} - t_{64}$$

$$* F_{2g}\ \psi_{27} = 4t_{69} + t_{64} - 2t_{62} + t_{60} + t_{55} - t_{53} + t_{51} - t_{48} - 2t_{44} - t_{41} - t_{37} + t_{30} - 2t_{27} + 4t_{25} + t_{23} - t_{20} + t_{18} - t_{16} - t_{11} - 2t_9 - t_7$$

$$F_{2g}\ \psi_{28} = 3t_4 - t_{14} - t_{22} - t_{32} t_{39} - t_{49} - t_{57} + 3t_{67}$$

$$F_{2g}\ \psi_{29} = t_6 - t_{65}$$

$$F_{2u}\ \psi_{30} = 4t_1 - t_3 - t_8 + t_{10} + 2t_{12} - t_{15} - t_{19} - 2t_{24} - 4t_{26} + t_{28} + t_{29} + t_{35} - t_{36} - t_{42} - t_{43} - 2t_{47} + t_{52} + t_{56} + 2t_{59} - t_{61} + t_{63} + t_{68}$$

$$* F_{2u}\ \psi_{31} = 4t_{70} - t_{68} - t_{63} + t_{61} + 2t_{59} - t_{56} - t_{52} - 2t_{47} - 4t_{45} + t_{43} + t_{42} + t_{36} - t_{35} - t_{29} - t_{28} - 2t_{24} + t_{19} + t_{15} + 2t_{12} - t_{10} + t_8 + t_3$$

$$F_{2u}\ \psi_{32} = 2t_2 + t_7 - t_{11} - t_{16} + t_{18} - t_{20} + t_{23} - 2t_{25} - t_{30} + t_{34} + \sum_{F_{2u}} (Ct)_{71-j}$$

Table 11. The Effect of S^2 on the Spin State Functions of the Eight Electron Problem

$S^2t_1 = 4t_1 + t_2 + t_3 + t_4 + t_5 + t_6 + t_7 + t_8 + t_9 + t_{16} + t_{17} + t_{18} + t_{19} + t_{36} + t_{37} + t_{38} + t_{39}$

$S^2t_2 = t_1 + 4t_2 + t_3 + t_4 + t_5 + t_6 + t_{10} + t_{11} + t_{12} + t_{16} + t_{20} + t_{21} + t_{22} + t_{36} + t_{40} + t_{41} + t_{42}$

$S^2t_3 = t_1 + t_2 + 4t_3 + t_4 + t_5 + t_7 + t_{10} + t_{13} + t_{14} + t_{17} + t_{20} + t_{23} + t_{24} + t_{37} + t_{40} + t_{43} + t_{44}$

$S^2t_4 = t_1 + t_2 + t_3 + 4t_4 + t_5 + t_8 + t_{11} + t_{13} + t_{15} + t_{18} + t_{21} + t_{23} + t_{25} + t_{38} + t_{41} + t_{43} + t_{45}$

$S^2t_5 = t_1 + t_2 + t_3 + t_4 + 4t_5 + t_9 + t_{12} + t_{14} + t_{15} + t_{19} + t_{22} + t_{24} + t_{25} + t_{39} + t_{42} + t_{44} + t_{45}$

$S^2t_6 = t_1 + t_2 + 4t_6 + t_7 + t_8 + t_9 + t_{10} + t_{11} + t_{12} + t_{16} + t_{26} + t_{27} + t_{28} + t_{36} + t_{46} + t_{47} + t_{48}$

$S^2t_7 = t_1 + t_3 + t_6 + 4t_7 + t_8 + t_9 + t_{10} + t_{13} + t_{14} + t_{17} + t_{26} + t_{29} + t_{30} + t_{37} + t_{46} + t_{49} + t_{50}$

$S^2t_8 = t_1 + t_4 + t_6 + t_7 + 4t_8 + t_9 + t_{11} + t_{13} + t_{15} + t_{18} + t_{27} + t_{29} + t_{31} + t_{38} + t_{47} + t_{49} + t_{51}$

$S^2t_9 = t_1 + t_5 + t_6 + t_7 + t_8 + 4t_9 + t_{12} + t_{14} + t_{15} + t_{19} + t_{28} + t_{30} + t_{31} + t_{39} + t_{48} + t_{50} + t_{51}$

$S^2t_{10} = t_2 + t_3 + t_6 + t_7 + 4t_{10} + t_{11} + t_{12} + t_{13} + t_{14} + t_{20} + t_{26} + t_{32} + t_{33} + t_{40} + t_{46} + t_{52} + t_{53}$

$S^2t_{11} = t_2 + t_4 + t_6 + t_8 + t_{10} + 4t_{11} + t_{12} + t_{13} + t_{15} + t_{21} + t_{27} + t_{32} + t_{34} + t_{41} + t_{47} + t_{52} + t_{54}$

$S^2t_{12} = t_2 + t_5 + t_6 + t_9 + t_{10} + t_{11} + 4t_{12} + t_{14} + t_{15} + t_{22} + t_{28} + t_{33} + t_{34} + t_{42} + t_{48} + t_{53} + t_{54}$

$S^2t_{13} = t_3 + t_4 + t_7 + t_8 + t_{10} + t_{11} + 4t_{13} + t_{14} + t_{15} + t_{23} + t_{29} + t_{32} + t_{35} + t_{43} + t_{49} + t_{52} + t_{55}$

$S^2t_{14} = t_3 + t_5 + t_7 + t_9 + t_{10} + t_{12} + t_{13} + 4t_{14} + t_{15} + t_{23} + t_{30} + t_{33} + t_{35} + t_{44} + t_{50} + t_{53} + t_{55}$

$S^2t_{15} = t_4 + t_5 + t_8 + t_9 + t_{11} + t_{12} + t_{13} + t_{14} + 4t_{15} + t_{25} + t_{31} + t_{34} + t_{35} + t_{45} + t_{51} + t_{54} + t_{55}$

$S^2t_{16} = t_1 + t_2 + t_6 + 4t_{16} + t_{17} + t_{18} + t_{19} + t_{20} + t_{21} + t_{22} + t_{26} + t_{27} + t_{28} + t_{36} + t_{56} + t_{57} + t_{58}$

$S^2t_{17} = t_1 + t_3 + t_7 + t_{16} + 4t_{17} + t_{18} + t_{19} + t_{20} + t_{23} + t_{24} + t_{26} + t_{29} + t_{30} + t_{37} + t_{56} + t_{59} + t_{60}$

$S^2t_{18} = t_1 + t_4 + t_8 + t_{16} + t_{17} + 4t_{18} + t_{19} + t_{21} + t_{23} + t_{25} + t_{27} + t_{29} + t_{31} + t_{38} + t_{57} + t_{59} + t_{61}$

$S^2t_{19} = t_1 + t_5 + t_9 + t_{16} + t_{17} + t_{18} + 4t_{19} + t_{22} + t_{24} + t_{25} + t_{28} + t_{30} + t_{31} + t_{39} + t_{58} + t_{60} + t_{61}$

$S^2t_{20} = t_2 + t_3 + t_{10} + t_{16} + t_{17} + 4t_{20} + t_{21} + t_{22} + t_{23} + t_{24} + t_{26} + t_{32} + t_{33} + t_{40} + t_{56} + t_{62} + t_{63}$

Table 11. Continued.

$$S^2 t_{21} = t_2 + t_4 + t_{11} + t_{16} + t_{18} + t_{20} + 4t_{21} + t_{22} + t_{23} + t_{25} + t_{27} + t_{32} + t_{35} + t_{41} + t_{57} + t_{62} + t_{64}$$

$$S^2 t_{22} = t_1 + t_5 + t_{12} + t_{16} + t_{19} + t_{20} + t_{21} + 4t_{22} + t_{24} + t_{25} + t_{28} + t_{33} + t_{34} + t_{42} + t_{58} + t_{63} + t_{64}$$

$$S^2 t_{23} = t_3 + t_4 + t_{13} + t_{17} + t_{18} + t_{20} + t_{21} + 4t_{23} + t_{24} + t_{25} + t_{29} + t_{32} + t_{35} + t_{43} + t_{59} + t_{62} + t_{65}$$

$$S^2 t_{24} = t_3 + t_5 + t_{14} + t_{17} + t_{19} + t_{20} + t_{22} + t_{23} + 4t_{24} + t_{25} + t_{30} + t_{33} + t_{35} + t_{44} + t_{60} + t_{63} + t_{65}$$

$$S^2 t_{25} = t_4 + t_5 + t_{15} + t_{18} + t_{19} + t_{21} + t_{22} + t_{23} + t_{24} + 4t_{25} + t_{31} + t_{34} + t_{35} + t_{45} + t_{61} + t_{64} + t_{65}$$

$$S^2 t_{26} = t_6 + t_7 + t_{10} + t_{16} + t_{17} + t_{20} + 4t_{26} + t_{27} + t_{28} + t_{29} + t_{30} + t_{32} + t_{33} + t_{46} + t_{56} + t_{66} + t_{67}$$

$$S^2 t_{27} = t_6 + t_8 + t_{11} + t_{16} + t_{18} + t_{21} + t_{26} + 4t_{27} + t_{28} + t_{29} + t_{31} + t_{32} + t_{34} + t_{47} + t_{57} + t_{66} + t_{68}$$

$$S^2 t_{28} = t_6 + t_9 + t_{12} + t_{16} + t_{19} + t_{22} + t_{26} + t_{27} + 4t_{28} + t_{30} + t_{31} + t_{33} + t_{34} + t_{48} + t_{58} + t_{67} + t_{68}$$

$$S^2 t_{29} = t_7 + t_8 + t_{13} + t_{17} + t_{18} + t_{23} + t_{26} + t_{27} + 4t_{29} + t_{30} + t_{31} + t_{32} + t_{36} + t_{49} + t_{59} + t_{66} + t_{69}$$

$$S^2 t_{30} = t_7 + t_9 + t_{14} + t_{17} + t_{19} + t_{24} + t_{26} + t_{28} + t_{29} + 4t_{30} + t_{31} + t_{33} + t_{35} + t_{50} + t_{60} + t_{67} + t_{69}$$

$$S^2 t_{31} = t_8 + t_9 + t_{15} + t_{18} + t_{19} + t_{25} + t_{27} + t_{28} + t_{29} + t_{30} + 4t_{31} + t_{34} + t_{35} + t_{51} + t_{61} + t_{68} + t_{69}$$

$$S^2 t_{32} = t_{10} + t_{11} + t_{13} + t_{20} + t_{21} + t_{23} + t_{26} + t_{27} + t_{29} + 4t_{32} + t_{33} + t_{34} + t_{35} + t_{52} + t_{62} + t_{66} + t_{70}$$

$$S^2 t_{33} = t_{10} + t_{12} + t_{14} + t_{20} + t_{22} + t_{24} + t_{26} + t_{28} + t_{30} + t_{32} + 4t_{33} + t_{34} + t_{35} + t_{53} + t_{63} + t_{67} + t_{70}$$

$$S^2 t_{34} = t_{11} + t_{12} + t_{15} + t_{21} + t_{22} + t_{25} + t_{27} + t_{28} + t_{31} + t_{32} + t_{33} + 4t_{34} + t_{35} + t_{55} + t_{65} + t_{69} + t_{70}$$

$$S^2 t_{35} = t_{13} + t_{14} + t_{15} + t_{23} + t_{24} + t_{25} + t_{29} + t_{30} + t_{31} + t_{32} + t_{33} + t_{34} + 4t_{35} + t_{55} + t_{65} + t_{69} + t_{70}$$

CONCLUSION

Energy levels have been calculated for the five molecular configurations. The square and the hexagon each have a bonding energy level; the tetrahedren has a non-bonding energy level, and the octahedren and cube have only anti-bonding levels.

The bonding levels for the square and hexagon are the same as those found in the literature which are obtained by the valence bond method. Thus, one may conclude that the spin state approach developed here is valid.

The non-bonding energy level of the tetrahedren is interesting. Because all exchange integrals vanish, the neglect of the overlap integral does not distort this result. Tetrahedral molecules do exist in nature (e.g., $B_4\ Cl_4$) so one would expect to obtain a bonding level. Additional lowering of this level might occur if one includes the multiple exchange and transfer integrals in the calculation. A separate calculation which includes the double exchange integrals for the tetrahedron has been made by the author. It is found that such terms do lower the energy in the tetrahedral case. Additional calculations involving the transfer integrals should be made to see how they contribute to the bonding.

For the octahedren and cube, the fact that the lowest levels are anti-bonding is inconclusive because of the neglect of the overlap integrals. However, the results indicate that the exchange integrals

are not responsible for bonding in these structures. Here again, calculations involving the overlap and transfer integrals should be made.

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